# A COMPARATIVE STUDY OF SULPHATE AND OXIDE COPPER-CHROME-ARSENIC (CCA) TREATMENT OF RADIATA PINE (*Pinus radiata* D. Don)

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## DECLARATION

**Except where otherwise indicated this thesis is my own work.**

**Ben Takavadiyi Mutandadzi.**

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## ABSTRACT

This study examines the treatment of *P. radiata* sawn timber using two commercial copper-chrome-arsenic (CCA) wood preservatives containing either copper sulphate or copper oxide. Timber is treated in a pilot scale pressure cylinder using a modified Bethell full cell process. Formation of chemical sludge by the CCA after treatment is analysed by evaporating aliquots of CCA solution removed from the pressure cylinder and weighing the sludge formed. Changes in the pH and the strength of $Cr^{III}$ leading to sludge formation in the reacted CCA solutions are measured using a pH meter and U.V. spectroscopy respectively and the chemical composition of the sludge is determined using atomic absorption spectrophotometry. The aim of this study is to quantify the process of sludge formation and to determine the chemical composition of the sludge for both the sulphate and oxide CCA preservatives. Secondly, the study aims to determine differences between the two preservative formulations with respect to susceptibility to sludging and also their suitability for use in a commercial pressure treatment plant.

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# CHAPTER 1

## 1. Introduction:

The decay of non-durable timber in ground contact and in marine environments can be largely prevented by application of wood preservatives. Penetration, to an appreciable depth, of preservatives toxic to wood destroying fungi, insects and marine borers is one of the main aims of wood preservation. An efficient wood preservative should be readily available and economic to use, permanent in service, safe and easy to apply, chemically stable and free from unpleasant odours.

In Australia, creosote or oil based preservatives have been extensively used for the pressure treatment of poles and posts but are unacceptable for many end uses, for example, in and around houses and in farm buildings. Alternatives to creosote include solvent borne compounds such as pentachlorophenol (PCP), metallic naphthenates, copper or zinc pentachlorophenates and water-borne preservatives such as copper-chrome-arsenic (CCA).

CCA is currently the most widely used preservative in Australia and over 3500 tons of dry salt equivalent were used in 1984 (Greaves 1984). The success of CCA's is due, in part, to the following;

. since they are water soluble, they can be transported in solid, powder or concentrated paste form and reconstituted prior to use.

. CCA treating solutions of differing strengths can be prepared on site, based on required retention per unit volume of wood.

. once the surface is dry, they leave treated wood in a clean condition which is pleasant to work with and to handle.
. treated wood can be painted over or decorated.
. they are free of obnoxious odours associated with some other preservatives.
. they can be combined with fire retardant chemicals.

Although CCA preservatives are widely used they do have the following disadvantages and unwanted effects:

. they may impair the mechanical strength of treated timber (Burmester and Becker 1963; Hager 1969; Bariska *et al.* 1988; Winandy and Boone 1988; Barnes and Winandy 1989) and plywood (Hutchinson *et al.* 1977; Vick 1980; Boggio and Gertjejansen 1982).
. treated timber may be prone to excessive checking (Belford 1968; Wilkinson 1979) and to collapse (McQuire *et al.* 1976).
. salt type CCA has a tendency to increase the electrical conductivity of treated poles (Clarke and Donaldson 1969) and to corrode treatment plant equipment (Hartford 1986) and galvanized hardware (Taylor 1981; Davis 1983).
. CCA preservatives have a tendency to form insoluble organo-metallic sludges in treatment plants (Cokley and Smith 1965; Rak and Clarke 1975; Mason and Sheard 1982; Pizzi *et al.* 1984; Hartford 1986).

The problem of excessive checking and splitting in CCA treated timber may be alleviated by treating wood with modified CCA formulations containing surfactants, emulsifiers, water repellents and structural and dimensional stabilizing agents such as polyethylene glycol and wax (Belford 1968) or by using an emulsion of CCA in oil (Protan = 35% oil, 65% water (Chin *et al.* 1986) or PROCCA (20% heavy oil and 80% water) (Schmalzl 1989 unpublished report). Recent developments in the U.S.A. and the U.K.

involve a commercial water repellent CCA - oil formulation called Ultrawood and a wax - CCA "pre-emulsion" respectively (Schmalzl 1989 unpublished report).

The sludging of CCA in treatment plants is relatively common (Cokley and Smith 1965; Rak and Clarke 1975; Mason and Sheard 1982; Pizzi *et al.* 1984; Hartford 1986) and can reduce plant efficiency by blocking sumps and pipes (Pizzi *et al.* 1984). Furthermore, since CCA sludge is relatively toxic (Cokley and Smith 1965; Rak and Clarke 1975; Winandy 1983; Pizzi *et al.* 1984) its disposal in an environmentally acceptable way may be costly. The simplest solutions to these problems is to prevent the initial formation of sludge through the use of modified CCA formulations or preservative practices. It has been suggested (Da Costa and Osborne 1968; Pizzi 1982; Hartford 1986) that oxide type CCA's are less prone to sludging than the conventional CCA type "C" formulation based on copper sulphate. In the U.S.A. a wax emulsion (1-2 % wax and paraffin) of CCA showed no sign of separation or sludging after six months of storage (Schmalzl 1989 unpublished report).

In this study sludge formation in oxide CCA and sulphate CCA formulations is compared. Initially sludge was examined in sulphate CCA solutions obtained from a commercial treatment plant treating radiata pine (*Pinus radiata* D.Don) but, subsequently, sludge formation was examined in the laboratory in greater detail in both sulphate CCA and oxide CCA solutions after treatment of radiata pine sapwood and heartwood in a pilot scale pressure plant.

The purpose of the study is twofold; firstly to assess quantitatively the process of CCA sludge formation and secondly to examine whether an oxide

CCA formulation is less susceptible to sludging than the conventional sulphate CCA type "C" formulation.

# CHAPTER 2

## Literature Review

### 2.1. Introduction to CCA preservatives and treatment methods:

Commercially, CCA preservatives are supplied in the form of dry salt, paste or liquid concentrate and are applied as aqueous solutions of 1.0 to 10.0 percent. These solutions have a pH of 1.6 to 3.0 (Belford and Nicholson 1968; Hartford 1986), and strong oxidizing properties due to the presence of hexavalent chromium ($Cr^{VI}$). CCA preservatives have a proven record of efficacy despite variation in the composition of different formulations and approximately 60% of the wood preservative market in Australia is comprised of CCA preservatives (Riley 1989 pers. comm.). In Europe about 3.8 million cubic metres of timber are treated with CCA salts, most of it in the U.K. (Schmalzl 1989 unpublished report).

### 2.1.1. Composition and formulation of CCA:

There are two main types of CCA preservative formulations; the salt type, type "S" (AWPA) or type "C (P)" sulphate CCA (Australian Standard; TPA), and the salt-free CCA commonly known as type "O" or oxide CCA. The major differences between the two formulations are as follows;

. Copper in the type "S" or "C (P)" formulations is present as pentahydrate copper sulphate ($CuSO_4.5H_2O$) but in the type "O" formulations it can be present as anhydrous copper oxide (CuO), hydroxide ($Cu(OH)_2$) or carbonate ($CuCO_3$).

. Chromium in the "S" type or "C (P)" formulation may be present as a dichromate salt of sodium ($Na_2Cr_2O_7.2H_2O$) or potassium ($K_2Cr_2O_7.2H_2O$) but in the type "O" formulation it is present as chromium trioxide ($CrO_3$).

. Arsenic in the "S" type or "C (P)" formulation is present as arsenic pentoxide ($As_2O_5.2H_2O$) while in the type "O" formulation it is present as arsenic acid ($H_4As_2O_7$).

. pH of commercially prepared type "S" solutions is between 2.0 and 2.3 while that for type "O" solutions is between 1.6 and 2.0.

### 2.1.2. Salt type CCA:

"Tanalith" CP is a salt - based CCA which is exclusively used for treating radiata pine timber in South Australia and the Australian Capital Territory (A.C.T), is supplied as a paste with the following composition ;

30% (w/w) $CuSO_4.5H_2O$ (Cu = 75.7 grams $kg^{-1}$),

38% $K_2Cr_2O_7.2H_2O$ (Cr=135.2 grams $kg^{-1}$)

17% $As_2O_5$ (As=95.8 grams $kg^{-1}$)

15% water ($H_2O$) .

The other commercial salt-type formulation, "Tanalith" C is supplied as a dry salt and has a similar chemical composition. About 95% of all CCA treatments in Australia use the salt-type CCA which is also commonly used in Europe, South Africa and New Zealand (Riley 1989 pers. comm.).

### 2.1.3. Salt free CCA:

Only 5% of all CCA treatments in Australia use "Tanalith" "O" type-C, oxide CCA (Riley 1989 pers comm.). It has the following composition:

24% CuO (Cu = 86.0 grams $kg^{-1}$)

40% $CrO_3$ (Cr = 147.9 grams $kg^{-1}$)

36% $H_4As_2O_7$ (As = 132.7 grams $kg^{-1}$)

Other salt-free formulations of commercial importance include Celcure and Boliden K33. The oxide CCA preservatives are not commonly used in Australia because they are more expensive to use ($30 - $35 per cubic metre of radiata pine treated to H4 hazard level) than the sulphate CCA ($20 - 25 per cubic metre (Riley 1989 pers comm.). In contrast to Australia, oxide CCA's are the most commonly used preservatives in the USA (Hartford 1986).

### 2.1.4. The application of CCA preservatives to wood:

The increased durability of timber treated with CCA preservatives is dependent *inter alia* on the depth of penetration, distribution, retention and fixation of the preservative. Australian Standard AS 1604-1980, for example, recommends penetration of all sapwood of treated radiata pine to ensure that no untreated sapwood is exposed during machining. Hardwoods such as spotted gum (*Eucalyptus maculata* Hook) poles used for overhead powerline supports should be penetrated to 25mm of sapwood or 75% of the sapwood depending on which is the greater (AS 2209, 1979).

Conventional methods for treating timber to achieve good penetration and retention of the preservative include;

. Bethell full cell treatment

. Lowry and Rueping's empty cell techniques

. Sap displacement or Boucherie treatment

All of these processes use mechanically applied pressure of up to 1380 kPa to penetrate timbers, including radiata pine with CCA preservatives. In some species, for example Sitka spruce (*Picea sitchensis* Bong. ) an even

penetration and distribution of the preservative may not be possible at these pressures due to the refractory nature of the wood. This impermeability arises due, in part, to structural features such as smaller and less frequent bordered pits and a greater proportion of aspirated pits (Liese and Bauch 1967). Fortunately, radiata pine is characterized by a large permeable sapwood band that can easily be impregnated with CCA preservatives. Since the treatment method used with CCA preservatives may affect the production of sludge, each process is briefly described.

#### 2.1.4.1. The Bethell full cell treatment:

The objective of full cell impregnation is to penetrate both cell walls and lumina so that absorption of the preservative at the end of the cycle is close to gross uptake, hence the term "full cell" which describes the condition of the wood cell after treatment. About 5% of gross uptake is recovered at the end of the treatment cycle (Wilkinson 1979). Since gross uptake depends primarily on void space, the timber must be seasoned to below fibre saturation point (FSP for radiata pine is between 28% and 32% moisture content), and preferably below 25% moisture content. A schematic diagram of a Bethell full cell treatment plant is shown in Fig. 2-1. The main components of the plant are:

. a pressure cylinder up to 2m diameter and 60m long fitted with a hydraulic door and door seal pump and a pressure relief valve.

. work tanks, mixing tanks and a "dirty water" tank.

. a vacuum pump, a pressure pump and a recirculation pump.

. a sump which collects run off from the drip pad and from the cylinder.

A full cell cycle commonly used for the commercial treatment of radiata pine (Fig. 2-2) involves six phases:

. initial vacuum of -90 kPa for 30 minutes (1) to remove air and water vapour from the timber.

. flooding of the cylinder with preservative while maintaining the vacuum (2)

. application of pressure of up to 1380 kPa until refusal (3) (refusal for radiata pine takes from 50 minutes to 90 minutes depending on the size of the charge and is defined as, when timber stops absorbing any more preservative solution or absorbs less than 1%, in ten minutes, of the total preservative pumped at 1380 kPa.)

. blow back or draining of the cylinder (4) using either the recirculation pump or the pressure phase of the vacuum pump. Although the latter is more rapid, it may lead to splashing of preservative if air is pumped into the work tanks at the end of blow back.

. final vacuum of -90 kPa for 30 minutes to remove excess preservative solution from the surface of treated timber (5)

. final blow back to empty the cylinder (6)

A normal cycle for the treatment of radiata pine takes between two to three hours depending on the size of the charge but treatment of refractory species may take up to 8 hours.

### 2.1.4.2. Empty cell treatments:

The Lowry and Rueping's empty cell techniques are similar to the Bethell treatment but do not use an initial vacuum. Hence, air in the wood, trapped and compressed during the schedule, expands rapidly after the pressure phase, expelling the preservative chemical from the wood cells. This phenomenon, technically known as 'kick back' forces about 60% of gross uptake of preservative out of the lumina leaving the cells almost empty while the cell walls are impregnated; hence the term "empty cell". About 60% of gross uptake of treating solution is forced back to the treatment cylinder.

### 2.1.4.3. The sap displacement method:

This technique which is commonly known as the Boucherie treatment is used in Europe (Evans *et al.* 1987) to treat some refractory timbers such as sitka spruce and Norway spruce (*Picea abies* Linn.) poles used for overhead line supports.* The treatment process is as follows; green poles are completely immersed in CCA in a conventional pressure cylinder under a pressure of about 1 000 kPa whilst a vacuum is applied to one end of the individual pole by means of metal sap displacement caps. Treatment lasts for about 40 hours and the extracted sap is recirculated with the preservative.

* The sap displacement method can be used to treat non refractory timbers at low pressures.

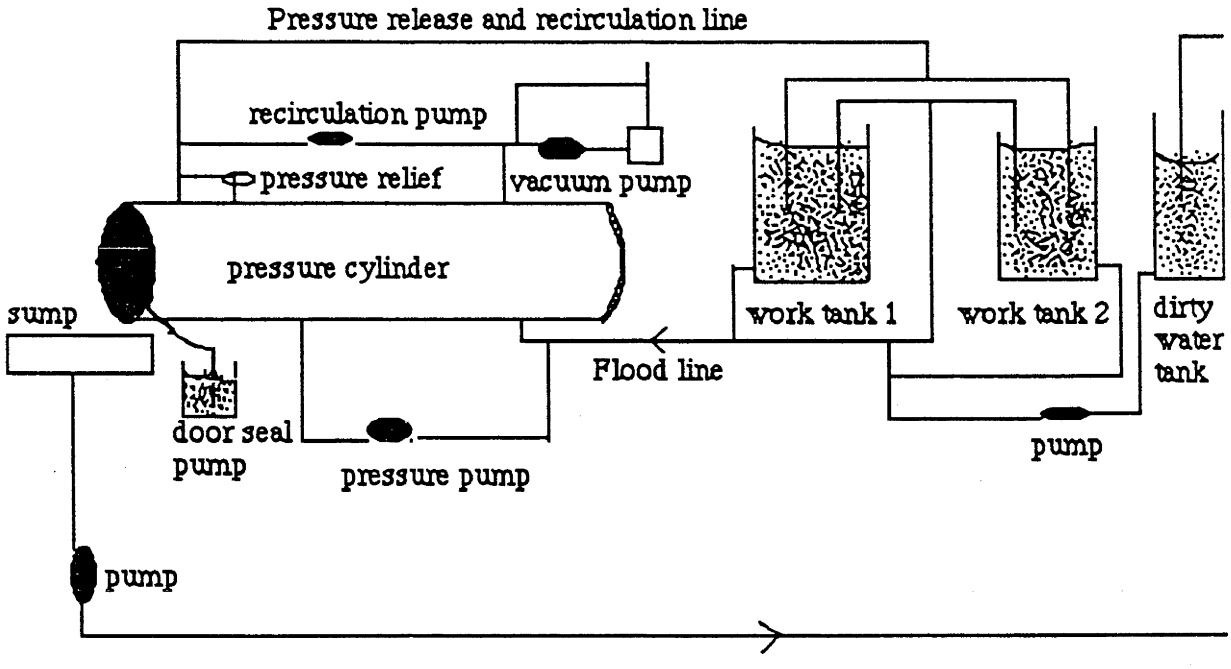


**Fig. 2-1: Schematic diagram of a Bethell full cell treatment plant**

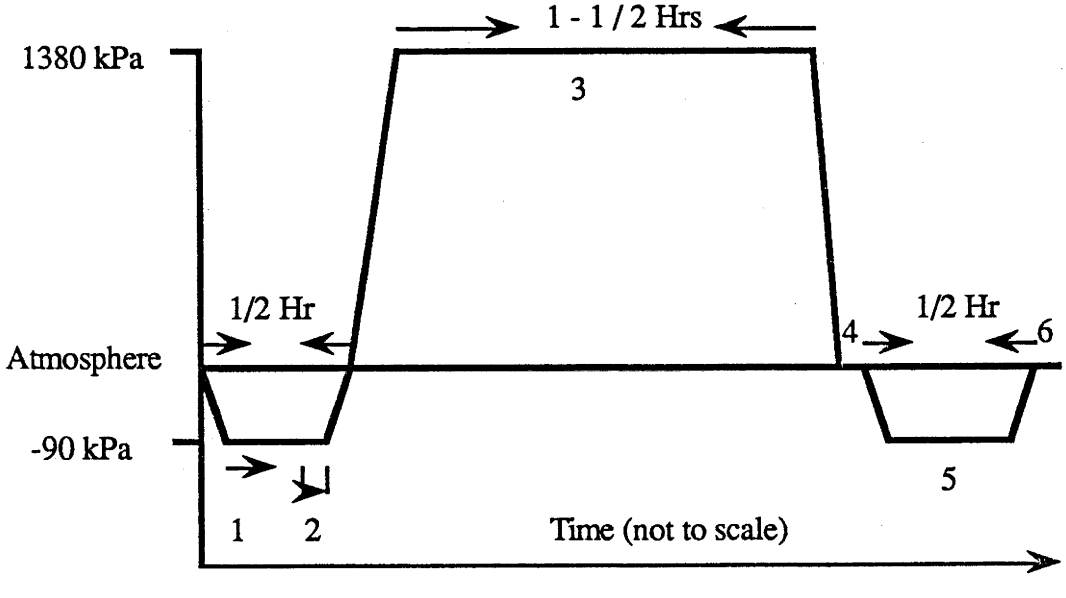


**Fig. 2-2: A Bethell full cell cycle**

## 2.2. Sludge formation in treatment plants:

CCA preservatives are the most widely used water borne preservative, but a major problem, which is of concern to the preservation industry and their regulatory bodies is the formation of organo-metallic sludges in treatment plants. These sludges form through the reaction of CCA with soluble organic components that are leached from the wood during treatment (Cokley and Smith 1965; Rak and Clarke 1975; Hartford 1986). In a treatment plant the largest source of sludge is from the sump and up to 2 tonnes of oven dry sludge can be collected annually from the sump of a plant having an annual throughput of 25 000 cubic metres of treated radiata pine roundwood (Riley and Fenning 1989, pers. comm.).

At treatment plants the occurrence of sludge can cause the following problems:

. loss of usable preservative.

. chemical imbalances in treating solutions that may result in an under treatment of subsequent charges (Pizzi *et al.* 1984).

. the necessity for periodic cleaning of the treating solution, sump and work tanks.

. a decrease in the efficiency of the treating plant and the effectiveness of the process. For example, over treatment can occur in the first charge and undertreatment in subsequent charges as the treating solution becomes out of balance (Pizzi *et al.* 1984).

. disposal problems since sludge is considered an environmental pollutant.

### 2.2.1. Composition of sludge and the process of sludge formation:

Metallic sludge is a dark green colour due to the presence of trivalent chromium ($Cr^{III}$) (McMahon, Hill and Koch 1942; Cokley and Smith 1965) but impurities in the sump including sawdust and soil particles can give sludge a pale brown colour. The chemical components of sludge are thought to be (McMahon, Hill and Koch 1942) ;

Chromium arsenate ($CrAsO_4$)

Copper chromate ($CuCrO_4$)

Copper arsenate ($Cu(OH)AsO_4$)

Chromium chromate ($Cr(CrO_4)_3$)

Chromium arsenates ($CrAsO_4$) are believed to be the major component of sludge which has an elemental composition of 75% chromium, 23% arsenic and traces of copper (2%) (Rak and Clarke 1975). Sludge analysed by Cokley and Smith (1965) contained an average of 40% arsenic. A 3% CCA solution reacted with pine sawdust extracts and stored for ten weeks gave a green sludge in which the main components were chromium and arsenic in a proportion of 1 Cr: 1.9 As (Eadie and Wallace 1962). Solutions recovered by vacuum at the end of a Bethell cycle (Pizzi *et al.* 1984) and left for 24 hours produced a sludge with molar proportions in the order of 3.13 $CrAsO_4$, 1.62 $CuCrO_4$, and 0.45 $Cu(OH)AsO_4$. Sludge also contains organic groups such as hydroxyls, aldehydes (McMahon, Hill and Koch 1942) and oxalates from the oxidation of extractives (Hartford 1986).

In a standard full cell treatment, sludge forms at ambient temperatures within a narrow range of solution strength between 2.0% and 2.5% (Cokley and Smith 1965), as a direct result of soluble wood components reacting with

the CCA solution. The treating solution can also be contaminated with corroded metal, sawdust and bark that provide aggregation points for the formation of chemical sludge. The process by which sludge forms is uncertain but it is thought (Hartford 1986) to result from the fixation reactions that normally convert CCA in solution to insoluble permanent residues within wood after treatment. Thus the process of sludge formation may be similar to the fixation of CCA in wood with the exception that the former occurs exterior to the treated wood while the latter presumably occurs within the void spaces present in wood (Schmalzl 1989 unpublished results). Studies on CCA fixation may thus provide a means of understanding the process of sludge formation.

### 2.2.2. Factors affecting the fixation of CCA to wood:

The fixation of CCA is a chemical reaction that renders copper, chromium and arsenic in wood resistant to leaching without greatly affecting their ability to prevent decay by wood degrading organisms. The process of fixation of CCA to wood was initially studied indirectly by reacting CCA with sawdust (Dahlgren and Hartford 1972) or model wood compounds such as D(+)-glucose, alpha cellulose, guaiacol or lignosulphonates (Pizzi 1981). The work of these authors looked at a number of factors influencing fixation such as temperature, pH, the reduction of $Cr^{VI}$ to $Cr^{III}$ and the composition of CCA solutions.

More recently, McNamara (1989) has studied the process of CCA fixation more directly by squeezing solutions of CCA from treated southern yellow pine blocks stored under different temperature regimes. Fixation was monitored by measuring the strength of $Cr^{VI}$ in the expressed solution using a chromotropic acid test.

Cooper and Ung (1989) also studied fixation of CCA in red pine under moderate temperature by squeezing the treated timber in a hydraulic press at 34 000 kPa. Fixation was measured by the chromotropic acid test and by visible light spectrophotometry at a wavelength of 580 nm. In accord with previous findings these studies concluded that fixation of CCA to wood is largely influenced by solution temperature and pH and the chemical composition of the treating solution.

#### 2.2.2.1. Temperature:

CCA fixation is highly temperature dependent (Cooper and Ung 1989) and the rate of chemical fixation of CCA in wood is accelerated when temperature is increased (Pizzi 1983). Thus total fixation of CCA occurs rapidly in treated wood after kiln drying (McNamara 1989). Accordingly, complete fixation, defined as "no detectable $Cr^{VI}$" requires about 20 days at 21°C in wood treated with CCA while the same degree of fixation can be obtained in about 12 hours at 50 - 60 °C (Cooper and Ung 1989). At 135 °C, fixation of CCA in western red ceder (*Thuja plicata* Donn.) and Douglas fir was complete in 10 minutes whereas at 27 °C fixation required 7 days (Feist and Ellis 1978) .

#### 2.2.2.2. pH:

A decrease in the initial pH of the CCA treating solution accelerates fixation in wood (Eadie and Wallace 1962; Pizzi 1983). Thus the lower pH of the $CrO_3$ based oxide CCA compared to the $Na_2Cr_2O_7$ based sulphate CCA should result in more rapid fixation. pH is also reported to affect the bonding of Cu, Cr and As to holocellulose and lignin, for example, the proportions of these elements complexing with holocellulose increases with decreasing pH from 5% at pH of 5 to 40% at pH 2 while their distribution on lignin decreases from 95% at pH 5 to 60% at pH 2 (Pizzi 1983).

### 2.2.2.3. Composition:

Of all CCA formulations tested (Hartford *et al.* 1982), the greatest fixation, measured by a leaching test, was found at a composition of; 17.8% CuO, 51.2% $CrO_3$ and 31.0% $As_2O_5$.

However, a composition of; 40.42% CuO, 34.26% $CrO_3$ and 23.5% $As_2O_5$ gave the highest performance index* against decay. There were slight indications that leaching was greater and performance poorer for the $K_2Cr_2O_7$ - based sulphate CCA formulations than the $CrO_3$ - based oxide CCA. In radiata pine, the distribution of copper, chrome and arsenic in the S2 layer of tracheids (1.0 : 2.8 : 0.8) was found to be closely related to the initial composition of the preservative (Ryan and Plackett 1987).

### 2.2.2.4. Time of fixation:

The reduction of $Cr^{VI}$ to $Cr^{III}$ which is one of the methods used by McNamara (1989) and Cooper and Ung (1989) to monitor the fixation process is thought to be a slow reaction taking place on the cellulose bonding sites following adsorption of chromic acid ($HCr_2O_7$) (Pizzi 1981). Inside wood, conversion of $Cr^{VI}$ to $Cr^{III}$ may commence within 72 hours of treatment (McNamara 1989). Complete fixation, defined as when 98% of the CCA is bound to the wood or when the concentration of $Cr^{VI}$ in solution reaches 15 PPM or less, may require between 14 days and 20 days (McNamara 1989). Some workers (Pizzi 1981; Hartford 1972;) have found that complete fixation at ambient temperature can take up to six weeks or more depending on the intensity of the conversion reactions in wood. These reactions may proceed slowly as long as some $Cr^{VI}$ and moisture are present in the treated wood, but below FSP conversion reactions stop as ion transport is hampered (Hartford 1972).

*Performance index was defined as 'Indices of condition (of decay and termite attack) over 12 years for panels treated with 13 different formulations of Cu-Cr-As and closely related compounds' (Fahlstrom 1978).

### 2.2.3. Stages of fixation of CCA to wood:

The three stages thought to be involved in fixation reactions are momentary initial reactions, primary fixation and conversion reactions (Dahlgren 1972; Pizzi 1981). Contact between the CCA solution and wood results in momentary initial reactions and an instant and extensive rise in pH due, in part, to a temporary adsorption of chromic acid ($HCr_2O_7$) onto cellulose binding sites and the subsequent depletion of protons ($H^+$) from the treating solution (Dahlgren 1972; Dahlgren and Hartford 1972; Pizzi 1981). Copper is fixed to the wood by ion - exchange with cellulose.

During primary fixation the three elements Cu, Cr and As are completely precipitated. The adsorbed $Cr^{VI}$ is reduced to $Cr^{III}$ which then complexes with arsenic to form ($CrAsO_4$) and with copper forming a copper chromate ($CuCrO_4$). These compounds may complex with lignin guaiacyl units (Pizzi 1983) or may remain in the voids present in wood as insoluble precipitates (Schmalzl 1989 unpublished data).

Conversion reactions involve pH changes due, in part, to the liberation and consumption of protons ($H^+$). This occurs when the unstable compounds formed during primary fixation are converted into thermodynamically stable compounds. The final equilibrium fixation products are thought to be; ion exchanged copper, $CrAsO_4$, Cu(OH), $CuAsO_4$ and $Cr(OH)_3$ (McMahon, Hill and Koch 1942; Dahlgren 1972).

The stages of fixation have been summarized by McNamara (1989) (Fig. 2-3). A rapid depletion of copper and chromium from the treating solution occurs one hour after treatment (Fig. 2-3), possibly due to preferential adsorption onto cellulose. This rapid change strips the treating solution of Cu and Cr and brings it out of balance. After four hours, depletion of copper and arsenic levels off. Although the depletion of arsenic from solution is

negligible in the first hour, it increases rapidly with time (Fig. 2-3) supporting the view that arsenic compounds are important fixation compounds (McMahon, Hill and Koch 1942; Cokley and Smith 1965; Pizzi *et al.* 1984).

## 2.3. Factors affecting sludge formation:

Although the process of sludge formation is probably similar to that of CCA fixation there is little published information available on the factors affecting sludge formation. Three factors which may affect formation of sludge during the treatment of timber with CCA preservatives include :

. % extractive content and types of extractives

. polysaccharide composition and resistance to chemical attack

. treatment conditions and the type of CCA solution (Fig. 2-4)

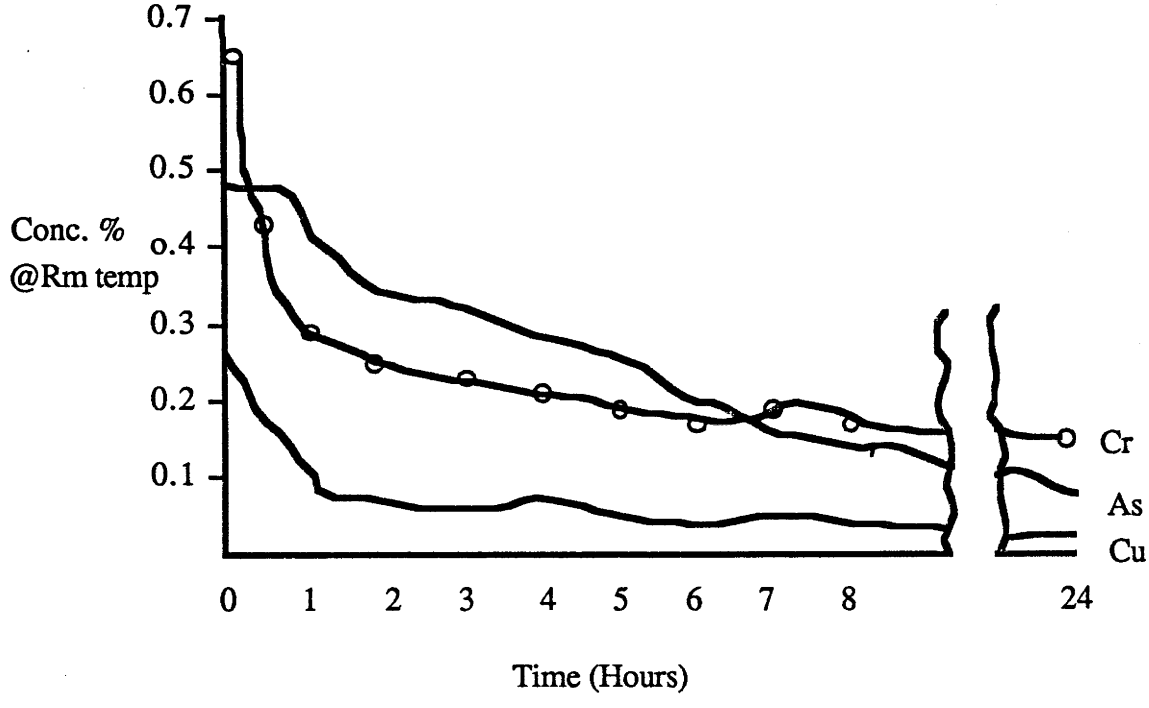


**Fig. 2-3: Fixation of CCA in Southern yellow pine (McNamara 1989)**

### 2.3.1. Effect of extractive content and types of extractives:

The nature of the wood substrate may affect sludging in the following ways;

(a) species with a low extractive content may be less prone to sludging since less organic matter is likely to be solubilised upon treatment.

(b) the type of extractives present may determine the extent of sludging.

(c) species resistant to impregnation may be less prone to sludging than permeable species since less extractives may be leached from the wood.

### 2.3.2. Effect of extractive content on sludging:

Wood is a polymeric blend of cellulose, hemicellulose, lignin and non-structural extractives. A major difference in the extent of sludging between species with dark coloured heartwood and pale coloured species (Cokley and Smith 1965) is attributed to a difference in extractive content. Hardwoods such as spotted gum when treated with a sulphate CCA solution cause more extensive sludging than softwoods (Cokley and Smith 1965).

Bark extracts generally contain much higher proportions of tannin and polyphenols (Chen 1982) than wood. For example, radiata pine bark contains up to 16 % (ODW) of extractives compared to 3.2% in sapwood (Yazaki 1983). Similarly the bole of Western hemlock (*Thuja heterophylla* Rafn.) has a total extractive content of 33.8% of which 29.3 % is from the bark and the water soluble fraction in bark is 4.9% compared to 0.8% in the wood.

Since the higher extractive content of bark could lead to more extensive sludging, round timber should be peeled to remove all bark. Prior to treatment with CCA, radiata pine round wood in the ACT (Fenning 1989 pers. comm.) is peeled to a depth of 5 to 10 mm to remove the inner bark

which is difficult to remove during conventional debarking. The removal of this layer probably has the effect of reducing sludging at the treatment plant but it also leads to a loss in recovery of some 30% or 6 000 cubic metres of wood per year for a plant with an annual throughput of 25000 cubic metres. Since the higher extractive content of bark could lead to more extensive sludging, round timber should be pealed to remove all bark.

The effects of extractives in causing sludging have been emphasized here but extractives probably play an important initial role in fixing CCA preservatives in wood by reducing the hexavalent chromium to the more reactive trivalent state. Recycling of CCA returns into solution wood extractives and also $Cr^{III}$ which has the effect of raising the pH to the threshold levels for sludge formation. Such effects have not been extensively studied, due in part to the complexity of wood extractives and the difficulty in isolating the compounds responsible.

Although there is little published information in this area there is some information that suggests that extractive type may affect sludging. For example hot water extractives of spotted gum give a brown sludge whereas gelatinous green sludge is produced by cold water extracts (Cokley and Smith 1965).

### 2.3.3. Effect of different types of extractives on sludging:

The primary wood extractives likely to be present in recycled CCA treatment solutions are the water and acid soluble fractions. Australian grown radiata pine sapwood or heartwood contains 5% of extractives in oven dry wood (ODW) (Smelstorius 1971), comprising of complex, low and high molecular compounds such as resins, tannins, polyphenols, essential oils, fats, fatty acids, carbohydrates and inorganic compounds. Of the total extractives present in radiata pine sapwood (5 %), the water soluble and acid soluble

fractions comprise 24 % ( 1.2% of the wood on an ODW basis, Harwood 1971; Smelstorius 1971) composed mainly of phenolic compounds, sugars and inorganic material.

The main water soluble phenols are phenolic glycosides. Sugars are primarily galactoglucomannan, arabinogalactan and traces of acidic xylan (Aspinall and Wood 1963) which yield glucose, mannose, galactose, arabinose and small amounts of xylose and rhamnose on hydrolysis. In radiata pine, the water soluble fraction varies from 6% of total extractives in the first 5 rings to 0.9% near the bark (Uprichard 1971). This suggests that heartwood may cause more sludging problems than sapwood particularly if sawn timber is treated. However, CCA preservatives do not penetrate heartwood to the same extent as sapwood during the treatment of round timber, hence extractives in heartwood may not be solubilised during treatment.

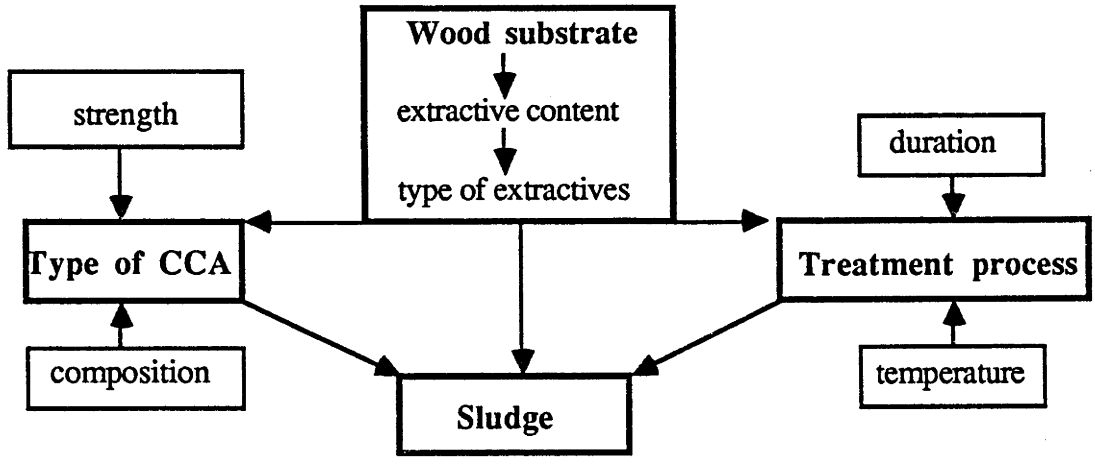


**Fig. 2-4: Factors affecting sludge formation under commercial conditions**

### 2.3.4. Polysaccharide composition and resistance to chemical attack:

The total polysaccharide content of radiata pine is 70.1% (ODW) calculated as 100 -(total lignin [24.9] + extractives[4.5] + protein [0.3] + ash [0.2]) (Smelstorius 1974). Hemicelluloses are the second most abundant wood component (20 - 30 % ODW) and the most water soluble of the polysaccharides. The three major components in pines are:

. galactoglucomannan (15 - 25%)

. arabinoglucuronoxylan (5 - 15%)

. arabinogalactan (< 1%)

The three hemicelluloses are made up of linear molecules of about 200 sugar units (Sjostrom 1981) which are easily hydrolysed to yield monosaccharides such as glucose. The percentage of monosaccharides derived from hemicelluloses of conifers and temperate hardwoods is given in Table 2-1. Free glucose, which is more abundant in hardwoods than conifers is also the most powerful reducing agent of the monosaccharides (Sjostrom 1981).

The literature on the resistance of wood to attack by chemicals is extensive (Meller 1963; Thompson 1969; Hillis 1976; Springler 1985). Coniferous species including radiata pine are generally more resistant than hardwoods to attack by acids, due primarily to their relatively lower pentosan to hexosan ratio (Meller 1963; Thompson 1969). For example, longleaf pine (*Pinus palustris* Mill.) with a pentosan content of 7.2% (Thompson 1969) and other southern pines are known for their resistance to acid degradation. Pine heartwood, in particular, is notable for its resistance to acid bisulphite treatment in pulp and paper manufacturing.

In contrast, hardwoods are characterized by a high pentosan content of up to 20% (ODW) (Springler 1985) and, therefore, sustain more degradation on exposure to acid hydrolysis although some hardwoods such as teak (*Tectona grandis* L.f.) and jarrah (*Eucalyptus marginata* Sm ) have a pentosan content comparable to softwoods and are resistant to chemical attack. Thus the polysaccharides in softwoods are probably less likely to be degraded, solubilised and form sludge during treatment with CCA than those found in hardwoods.

### 2.3.5. Treatment conditions affecting sludge formation:

Although the process of sludge formation may be related to the fixation of CCA preservatives it may also be affected by plant operating procedures and general yard hygiene. For example, overnight soaking of timber in CCA is not recommended as it can cause solubilisation of extractives and extensive sludging and the formation of surface deposits on the treated timber (Evans 1989 pers. comm.). To avoid sludging, timber to be treated should have clean surfaces free of bark, soil and sawdust. A 25 or 50 micron filter attached to the recirculation pump circuit can ensure that a clean solution is used for treatments (Koppers - Hickson Inc., Technical information 1978). Other factors thought to contribute to sludging such as water hardness and corrosion of equipment are more difficult to control but hosing down the pressure cylinder with clean, cold water may alleviate sludging problems arising from corrosion (Hartford 1986).

#### 2.3.5.1. Treatment process:

Since the acidic CCA solution is in contact with the wood for over two hours during a Bethell full cell treatment, some soluble components of the wood leach into the preservative solution in the treatment cylinder. Subsequently these soluble wood components are pumped back to the work tanks along

with the preservative during the final blow back. An increase in the concentration of soluble wood components may result in the formation of sludges in the work tanks. Sludge also builds up in the dirty water tank, mixing tank and in the pipes where it can cause blockages and affect the normal operation of the pressure pump.

Because chemical fixation reactions occur between the preservative and the wood during impregnation, when pressure is released the expelled solution ("kick back") is selectively stripped of preservatives so that the ratio of copper, chromium and arsenic is very different from that of the original solution (McMahon, Hill and Koch 1942). A large "kick back" resulting from an empty cell treatment returns to the treating cylinder relatively larger amounts of soluble organic matter than the full cell treatments. Accordingly, empty cell treatments generally cause more extensive sludging than full cell treatments and thus they are not suitable for use with CCA preservatives (Wilkinson 1979).

The sap displacement method or Boucherie treatment requires prolonged contact between CCA and green wood (up to 40 hours in commercial treatments) which may lead to greater removal of soluble wood components than in conventional treatment methods. In addition, since sap removed during treatment is recirculated with preservative, excessive sludging can occur (Mason and Sheard 1982). However, the extent of sludging can be reduced by using weaker CCA treating solutions (Evans 1989 pers. comm.).

Steam pre-treatment exacerbates sludging (Groves 1989 pers. comm.) since water soluble extractives are leached which are subsequently hydrolysed to yield monomeric sugars such as glucan, xylan and araban from the wood and these then react with the CCA to form sludge during treatment (Kubinsky and Ifju 1973).

### 2.3.5.2. Temperature:

The water soluble fraction in softwoods and hardwoods can be increased by as much as 10% by using boiling water (Herrick and Hergert 1976). Increased temperatures and lower pH of treatment solutions increase the rate of hydrolysis of wood polysaccharides. An increase in temperature by 10°C, for example, doubles the rate at which wood is degraded by acids (Thompson 1969) while an increase in acidity of the degrading chemical increases the $H^+$ activity.

Sludge formation increases significantly in treating plants when the cylinder and charge temperatures increase as a result of seasonal fluctuations in temperature (Cokley and Smith 1965). Similarly, sludging is more extensive in the tropics than in temperate regions (Wilkinson 1979). For example, the CCA treatment of radiata pine in the ACT causes less sludging than in plants located in the south coast of NSW since the former is at an elevated altitude and has relatively low mean ambient temperatures (Fenning 1989 pers. comm.), whereas the latter has a humid subtropical climate.

Storage temperature is important in determining the rate of $Cr^{VI}$ reduction and sludge formation. CCA treating solutions stored at 4 °C are less likely to sludge than those stored at room temperature (Rak and Clarke 1975; Mason and Sheard 1982). Lower temperatures may be realised by insulating storage tanks or using cooling coils (Evans 1989 pers comm.). Treating solutions stored at a lower temperature also afford better penetration and retention of CCA and cause less corrosion (Hartford 1986).

**Table 2-1: Frequency of monosaccharides after acid hydrolysis of wood**

| Monosaccharide | Conifers (% of total) | Temperate hardwoods (%) |
|---|---|---|
| D - glucose | 61 - 65 (includes cellulose) | 57 - 73 |
| D - mannose | 7 - 16 | 0.3 - 4.0 |
| D - galactose | 6 - 17 | 1 - 4 |
| D - xylose | 9 - 13 | 20 - 39 |
| L - arabinose | 3.5 | 1 |
| L - rhamnose | 1 | 1 |
| L - fucose | 1 | 1 |

**After Doimo 1984**

### 2.3.5.3. Duration of treatment:

Sludging of CCA solutions is in proportion to the duration of treatment (Pizzi *et al.* 1984; Hartford 1986) but as yet it cannot be totally eradicated. However, it may be minimized by shortening the treating cycle, assuming adequate penetration and retention can still be achieved, by eliminating the final vacuum phase of a full cell treatment.

### 2.3.5.4. Effects of CCA type:

The effects of different formulations of CCA on sludging has not been established and there is little published information on the subject. However, it has been suggested (Pizzi 1981; Hartford 1986) that salt-free or

oxide CCA solutions are less prone to sludging than their salt type or sulphate counterparts due to their lower initial pH. In commercial practice, the average pH at which sludging occurs is 2.3 (Hartford 1986) and thus it is possible that oxide CCA (Minimum pH 1.6 at strength 1.02% ) may sludge less than the sulphate CCA (minimum pH 2.0 at 1.18 to 2.2%).

Generally, the oxide CCA contains relatively higher levels of arsenic ($H_4As_2O_7$) which, because of their acidity, are less likely to form sludge (Mason and Sheard 1982). In the USA, (Hartford 1986) prohibition of the manufacture and sale of CCA formulations containing sulphate ions has been recommended due to problems of corrosion, sludging and formation of sodium or potassium salts on the surface of treated timber. Although surface deposits may be absent from oxide CCA treated timber, their relatively high acidity can promote corrosion and it has been suggested (Hartford 1986), that the lower limit of pH of oxide CCA should be increased from 1.6 to 1.67.

## 2.4. Concluding summary:

The literature reviewed in this study has suggested that the process of sludge formation is related to the process of fixation of CCA preservatives. Some operational and environmental problems arising from the formation of sludge have also been highlighted. Treatment process (extent of "kick back") and treatment time have been regarded as major determinants of the extent of sludging as they determine the amount of soluble wood components that can be leached into the acidic CCA. Timber species could also be a major determinant of the extent of sludging as some timbers contain more of the easily solubilised compounds than others but this subject area has received little attention.

From this review it is also apparent that there is little information available concerning the chemical changes that take place in solutions which have been removed from treated wood by the final vacuum, or the quantity of sludge formed during storage of these solutions. Furthermore, it appears that little information is available regarding the effect of CCA formulation on sludge formation. This work in this thesis will be one of the first studies to examine the differences between CCA formulations with respect to their susceptibility to sludging. The work initiated by Rak and Clarke (1975) on composition of CCA solutions with respect to chemical stability and sludging will also be extended in this study.

# CHAPTER 3

## Sludge formation in a commercial treatment plant

### 3.0 Introduction:

In Australia, "Tanalith" CP sulphate CCA salt formulations are the most commonly used water-borne wood preservatives for the full cell treatment of radiata pine and some hardwoods such as spotted gum. However, after treatment there is sometimes a problem of organo-metallic sludge formation as a result of the leaching and reaction of soluble wood components with the treatment solution. Soluble wood components reduce the more chemically stable hexavalent chrome ($Cr^{VI}$) in CCA to the less stable and more chemically reactive trivalent chrome ($Cr^{III}$). These reactions lead to a substantial rise in the pH of the treating solution and the formation of insoluble metal complexes (Rak and Clarke 1975).*

Although, at present, the occurrence of sludge cannot be totally eradicated from treatment plants it should be controlled as sludge imposes additional economic and environmental costs on the wood preservation industry. For example, usable preservative can be lost through sludge formation and this can lead to undertreatment of subsequent charges. Since sludge is a toxic waste which contains up to 40 % of arsenic (w/w) (Cokley and Smith 1965; Pizzi *et al.* 1984) additional costs are also involved in its safe disposal. A major drawback to reducing the production of sludge at treatment plants, however, is that the formation of sludge is not well understood.

*Wood has a pH of around 4-5 and therefore contact between timber and CCA may also cause an increase in the pH of CCA during treatment although there is no published information to substantiate this.

The aim of the work in this chapter, therefore, is to quantitatively examine the formation of sludge in a commercial treatment plant. The study used commercial CCA solutions obtained from a plant treating radiata pine round timber.

## 3.1. Materials and methods:

### 3.1.1 The treatment plant:

The plant, which is owned by Koppers - Hicksons Australia Pty Ltd, is situated in the Hume industrial area of the Australian Capital Territory (A.C.T.) about 5 km south of Canberra. It has an annual throughput of 25000 cubic metres of radiata pine roundwood, mainly first thinnings from the Tumut and A.C.T. forest regions. The pressure cylinder is 30.5 m long x 1.37 m in diameter connected to two work tanks each with a holding capacity of 75 000 litres of CCA preservative. The work tanks are fed from a 35 000 litre dirty water tank and a 25 000 litre mixing tank. An average of three charges (18 cubic metres of wood per charge) are run every day and each charge takes approximately three hours to complete. A full cell cycle is used and is completely automated with a Hewlett Packard programmed computer equipped with a printer and a Festo timing computer. Gross absorption of CCA by each charge averages 9 000 litres. The volume of solution resulting from the final vacuum is about 250 litres. The same volume of solution also arises from kick back when pressure is released.

Each year about 2 tonnes (oven dry basis) of sludge is removed from the sump and from the dirty water tank (Reily 1989 pers. comm.). The sludge is stabilized by mixing with cement and encapsulating it in a concrete water pipe. Disposal of the sludge is by burial of the pipes at an approved landfill.


Fig. 3-0: Varian Spectr AA atomic absorption spectrophotometer

### 3.1.2 Collection of CCA solutions:

Sulphate CCA solution arising from drips after treatment of radiata pine rounds was collected in 100, 50 ml graduated plastic sample tubes (Opticul 2070 polypropylene tubes). Tubes were filled to the 40 ml mark and then transported to the laboratory for investigation.

### 3.1.3 Analysis of trivalent chrome ($Cr^{III}$) in CCA solutions:

At a wavelength between 565 nm and 600 nm $Cr^{VI}$, $Cu^{2+}$ and $SO_4^{2-}$ ions show a minimum absorbance of ultraviolet (u.v.) light (Rak and Clarke 1975). At a wavelength of 595 nm $Cr^{III}$ ions show maximum absorbance (Pizzi 1981) and the increasing strength of $Cr^{III}$ ions in solution has a direct relationship with absorbance (Rak and Clarke 1975). Arsenic compounds do not absorb u.v. light (Rak and Clarke 1975).

A 1.9% "Tanalith" CP, CCA treating solution was prepared in the laboratory by accurately weighing 24 grams of CCA concentrate (80% w/w) on a Mettler electronic balance (PM 15) and dissolving it in 1000 ml of tap water (tap water is used for commercial CCA preparations) in a 1 litre volumetric flask. Ten, 50 ml sample tubes were then filled to the 40 ml mark with this solution and analysed for copper and chromium using a Varian Spectr AA atomic absorption spectrophotometer (Fig. 3-0) (Williams 1972). The samples contained an average of 5.692 ppm or 3.86 grams $l^{-1}$ of $Cr^{VI}$ (approximately 0.1545 grams in 40 mls). This analysis indicates that the solution strength of the Tanalith CP solution prepared above was 2.4% rather than 1.9%. This discrepancy may have occurred due to variation in the solution strength of the concentrate used to prepare the Tanalith CP solution.

Using AnalaR chromium potassium sulphate or chrome alum ($CrK(SO_4)_2.12H_2O$) and AnalaR potassium dichromate ($K_2Cr_2O_7.2H_2O$) as sources of $Cr^{III}$ ions and $Cr^{VI}$ ions respectively (Rak and Clarke 1975),

separate solutions (20 mls each) of increasing $Cr^{III}$ ions and decreasing $Cr^{VI}$ ions (Table 3-1) were prepared by accurately weighing the salts and mixing with tap water. Solutions containing the $Cr^{III}$ and $Cr^{VI}$ ions were then mixed to produce a total chromium content in the resulting 40 ml mixture of approximately 0.1545 grams. To each 40 ml chromium solution 0.3498 grams of pentahydrate copper sulphate ($CuSO_4.5H_2O$) was then added. U.V. absorbance was measured using a Unicam SP 1800 U.V. Spectrophotometer equipped with a pair of Thermal Syndicate precision optical cells. Tap water was used in the reference cell and u.v. measurements were taken at 595 nm wavelength. A calibration curve of $Cr^{III}$ strength against u.v absorbance (Figure 3-1) was produced which was then used to follow the conversion of $Cr^{VI}$ to $Cr^{III}$ during sludging in the treatment solution.

### 3.1.4 Yield of $Cr^{III}$, pH changes and the point of sludging:

The build up of $Cr^{III}$ in the treatment solution was determined by u.v. spectroscopy measurements taken every half hour up to the precipitation point where sludge began to form. Changes in pH of the treatment solution were also determined using an Activan BJ 312 refillable glass electrode pH meter which was standardized to read pH measurements ranging from pH 1.00 to 4.00.

### 3.1.5 Quantity of sludge formed:

A point was reached when u.v measurements could no longer be taken as absorbance was so high that readings went off scale. At this point, hereafter referred to as the 'precipitation point', sedimentation of the CCA solution occurred and all sample tubes had similar amounts of precipitation (sludge). This sludge was then collected by shaking the sample tubes and then centrifuging them at 6000 RPM for ten minutes in an MSE Multex centrifuge. The resultant supernatant solutions

(to minimize further formation of sludge)
were stored in the refrigerator at 4 °C and then analysed for their elemental
mposition using atomic absorption spectrophotometry (Williams 1972). The green sludge was washed with distilled water and centrifuged again for ten minutes. The sludge was dried at room temperature over nitrogen (to minimize oxidative changes in the sludge) in a Pierce Reacti Therm evaporating module by passing compressed nitrogen gas through injectors placed in the sample tubes. Further drying was achieved in a desiccator under vacuum using anhydrous sodium chlorite crystals. After drying, the weight of the sludge in each tube was measured on a balance (Ainsworth AL-300). The quantity of sludge formed in 5 replicate 40 ml solution was initially measured on a six hourly basis up to 90 hours then on a weekly basis up to eight weeks.

### 3.1.6 Determination of chemical composition of the sludge:

After weighing, the sludge was digested by adding 2 mls of 98% AnalaR sulphuric acid ($H_2SO_4$) followed by 10 mls of distilled water. Both the supernatant solution and the sludge solution were then analysed after dilution with deionized water for copper, chrome and arsenic by atomic absorption spectrophotometry (Williams 1972).

**Table 3-1: Proportions of $Cr^{III}$ and $Cr^{VI}$ in the calibration solution:**

| Trivalent Chrome (Chrome Alum) | | Hexavalent Chrome (Dichromate) | |
|---|---|---|---|
| Molar ratio | Grams per 20 mls | Molar ratio | Grams per 20 mls |
| 0.00 | 0.0000 | 0.074 | 0.1539 |
| 0.01 | 0.0104 | 0.069 | 0.1435 |
| 0.02 | 0.0208 | 0.064 | 0.1331 |
| 0.03 | 0.0312 | 0.059 | 0.1227 |
| 0.04 | 0.0416 | 0.054 | 0.1123 |
| 0.05 | 0.0520 | 0.049 | 0.1019 |
| 0.06 | 0.0624 | 0.044 | 0.0915 |
| 0.07 | 0.0728 | 0.039 | 0.0811 |
| 0.08 | 0.0832 | 0.034 | 0.0707 |
| 0.09 | 0.0936 | 0.029 | 0.0603 |
| 0.10 | 0.1040 | 0.024 | 0.0499 |
| 0.11 | 0.1144 | 0.019 | 0.0395 |
| 0.12 | 0.1248 | 0.014 | 0.0291 |
| 0.13 | 0.1352 | 0.009 | 0.0187 |
| 0.14 | 0.1456 | 0.004 | 0.0083 |
| 0.15 | 0.1560 | 0.000 | 0.0000 |

## 3.2 Results:

### 3.2.1 Formation of $Cr^{III}$ in reacted CCA solutions:

At a wavelength of 595 nm, $Cr^{III}$ concentration in controls showed a linear relationship with absorbance (Fig. 3-1), in accord with the findings of Rak and Clarke (1975). In reacted CCA solutions, obtained from the treatment plant, determination by u.v. spectroscopy of $Cr^{III}$ content showed a progressive increase in the formation of $Cr^{III}$ until the strength of $Cr^{III}$ in the treating solution reached 1.5 grams $l^{-1}$ (Fig. 3-2). At that point, a heavy precipitation occurred so that no further u.v. measurements could be taken. Sedimentation followed and a green sludge began to collect at the bottom of the sample tubes.

### 3.2.2 pH changes in reacted CCA solutions:

The pH of the reacted CCA treatment solution rose initially from 2.08 to 2.36 in the first hour after treatment (Fig 3-3), reaching 3.26 after 6 hours when sludge began to form. After 2 weeks, the pH of the solution approached 4.00 but then the formation of sludge was essentially complete. The critical pH for sludge formation in the treating solution was 3.26 (Fig. 3-3).

### 3.2.3 Weight of sludge formed:

Although sludging was more intense in the first 48 hours after treatment, the rate at which it was formed dropped considerably from about 0.07 grams $l^{-1}$ $hr^{-1}$ in the first 6 hours after precipitation to 0.03 grams $l^{-1}$ $hr^{-1}$ during the next 6 hours and then to 0.02 grams $l^{-1}$ $hr^{-1}$ during the remaining 36 hours (Fig. 3-4). Between 48 hours and 90 hours the amount of sludge formed fluctuated (Fig. 3-4). During the eight week storage time the rate at which sludge formed dropped from 0.054 grams $l^{-1}$ $wk^{-1}$ in the first week to 0.034

grams $l^{-1}$ $wk^{-1}$ in the second week (Fig. 3-5). As long as the pH of the treating solution continued to rise steadily, increasing amounts of sludge were collected. After two weeks of storage the rate of change in pH became negligible and sludge formation was essentially complete (Fig. 3-5).

### 3.2.4 Chemical composition of the sludge:

The green sludge, when analysed by atomic absorption spectrophotometry at six hourly intervals during sludging, had an average composition of 20 % arsenic, 10 % chromium, 3 % copper and 67 % salts, probably sulphates and oxalates. Sludge formed in the first 6 hours is composed largely of arsenic and chromium but after 18 hours copper is present in the sludge (Table 3-3). The content of copper in the sludge remained constant at 0.025 grams $l^{-1}$ during the 90 hours of laboratory investigation but increased slightly during the eight week storage time.

### 3.2.5 Composition of the CCA solution prior to and during sludging:

The reactions prior to sludging result in the treating solution being "out of balance" by removing a large proportion of arsenic. For example, the proportion of arsenic in the treating solution falls from 26.7 % to 22.6 % after sludging (Table 3-2). In contrast the relative proportions of copper and chromium rise initially but then remain relatively constant after 12 hours.

Sludging is preceded by a rapid depletion of arsenic and chromium from the treatment solution (Fig. 3-6) suggesting that the initial precipitation is mainly a chromium arsenic complex. However, the rate of removal of arsenic from solution before sludging is initially higher than chromium (Fig. 3-6). Following sludging, the situation is reversed so that chromium is depleted more rapidly than arsenic. This is in accord with Rak's and

Clarke's observations (1975) of a saturation point of $Cr^{III}$ in the ionizing acid media as a result of a common ion effect, in this case, with arsenic. Movement of copper from solution is medium (Fig. 3-6) suggesting that it is not initially a significant component in the initial formation of sludge.

However, the rate of removal of copper from solution after 12 hours is similar to the removal of chromium, suggesting that copper may be incorporated into the Cr / As compounds at a later stage of sludging.

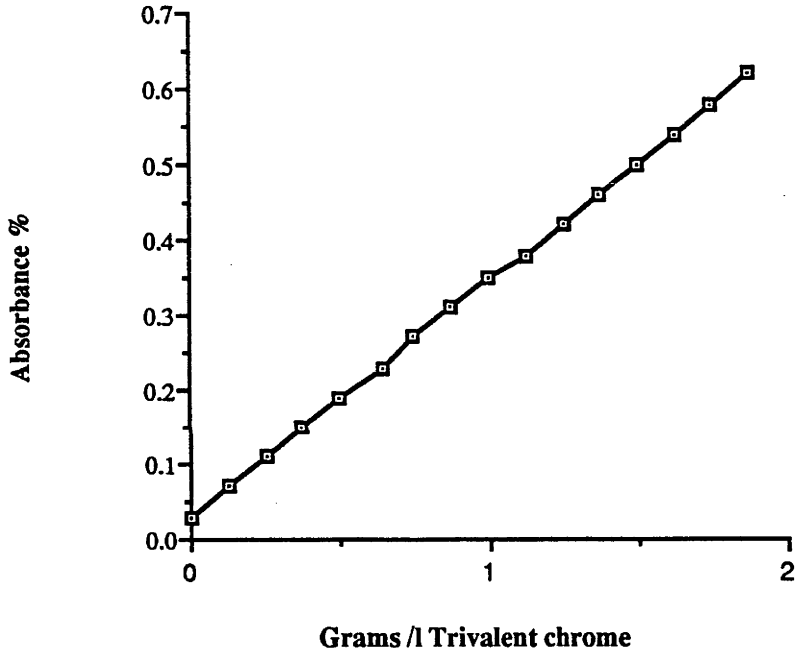


**Fig. 3-1: Calibration of $Cr^{III}$**

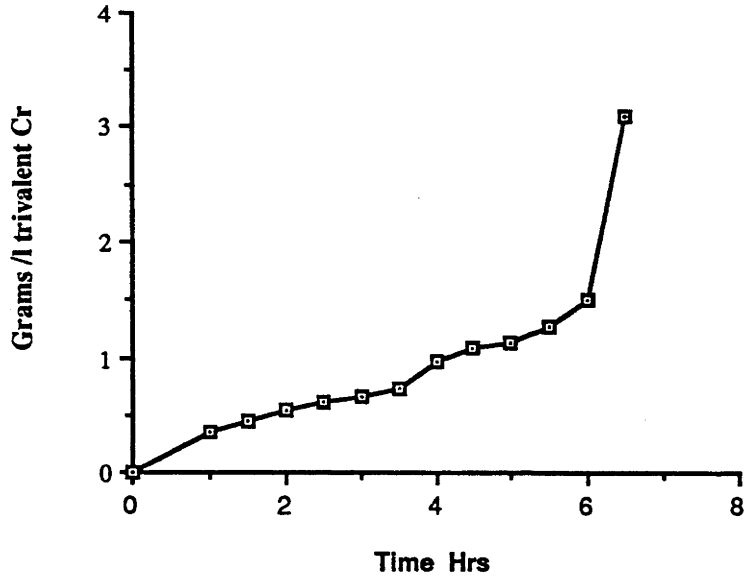


Fig. 3-2: Saturation point for $Cr^{III}$ ions

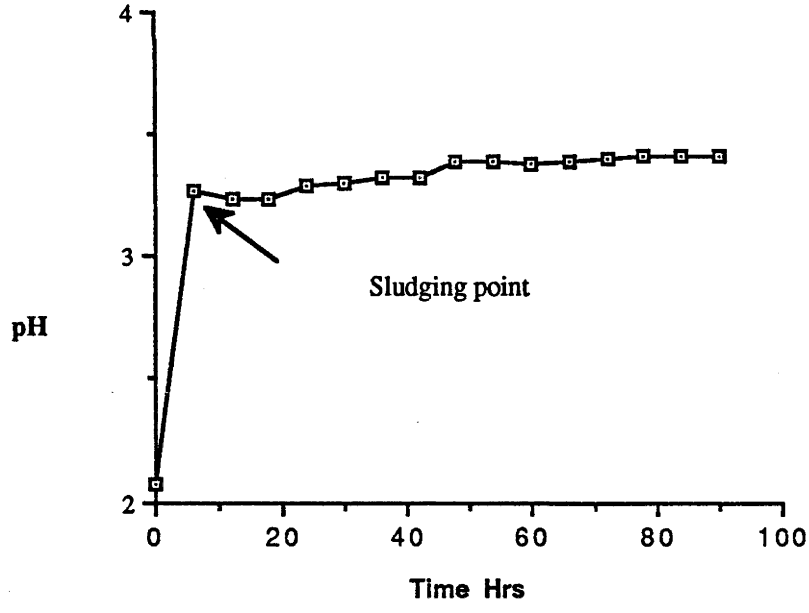


Fig. 3-3: Critical pH for sludging

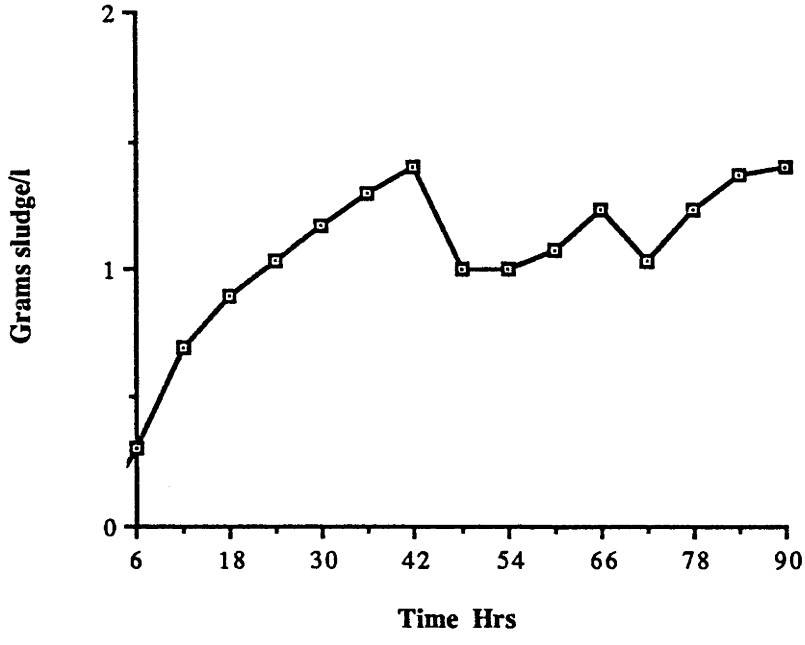


Fig. 3-4: Quantity of sludge formed in tubes after storage (6 - 90 hrs)

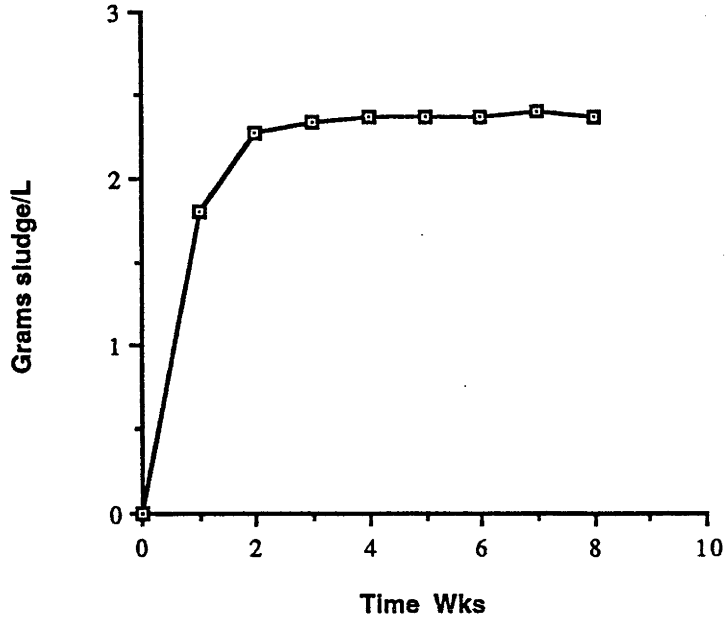


Fig. 3-5: Quantity of sludge formed in tubes after storage (1 - 8 wks)

**Table 3-2: Proportions of Cu, Cr and As in solution during sludging**

| Time (Hours) | % Cu | % Cr | % As |
|---|---|---|---|
| 0 | 26.7 | 46.6 | 26.7 |
| 12 | 30.3 | 47.7 | 22.6 |
| 24 | 30.4 | 49.1 | 21.1 |
| 36 | 30.5 | 49.1 | 20.4 |
| 48 | 29.3 | 47.6 | 21.3 |
| 60 | 31.6 | 49.2 | 19.8 |
| 72 | 31.3 | 50.0 | 18.7 |
| 84 | 31.4 | 48.4 | 19.5 |

**Table 3-3: Variation in the chemical composition of sludge**

| Wt. of sludge analysed (g) | Time of formation (Hours) | Wt.Cu (g) | Wt.Cr (g) | Wt As (g) | % Cu | % Cr | % As |
|---|---|---|---|---|---|---|---|
| 0.30 | 6 | 0.00 | 0.03 | 0.03 | 0.00 | 11.0 | 11.1 |
| 0.70 | 12 | 0.00 | 0.05 | 0.07 | 0.00 | 10.2 | 16.5 |
| 0.90 | 18 | 0.03 | 0.10 | 0.17 | 3.70 | 11.1 | 18.5 |
| 1.03 | 24 | 0.03 | 0.10 | 0.17 | 3.20 | 9.7 | 16.1 |
| 1.17 | 30 | 0.03 | 0.10 | 0.20 | 2.90 | 8.6 | 17.1 |
| 1.30 | 36 | 0.03 | 0.10 | 0.20 | 2.60 | 7.7 | 15.4 |
| 1.40 | 42 | 0.03 | 0.10 | 0.20 | 2.40 | 7.1 | 14.3 |
| 0.96 | 48 | 0.03 | 0.13 | 0.20 | 3.40 | 13.8 | 20.7 |
| 0.96 | 54 | 0.03 | 0.10 | 0.17 | 3.40 | 10.3 | 17.2 |
| 1.06 | 60 | 0.03 | 0.13 | 0.20 | 3.10 | 12.5 | 18.8 |
| 1.23 | 66 | 0.03 | 0.13 | 0.27 | 2.70 | 10.8 | 21.6 |
| 1.03 | 72 | 0.03 | 0.17 | 0.30 | 3.20 | 16.1 | 29.0 |
| 1.23 | 78 | 0.03 | 0.17 | 0.30 | 2.70 | 13.5 | 24.3 |
| 1.37 | 84 | 0.03 | 0.17 | 0.30 | 2.40 | 12.2 | 22.0 |
| 1.40 | 90 | 0.03 | 0.20 | 0.33 | 2.40 | 14.3 | 23.8 |

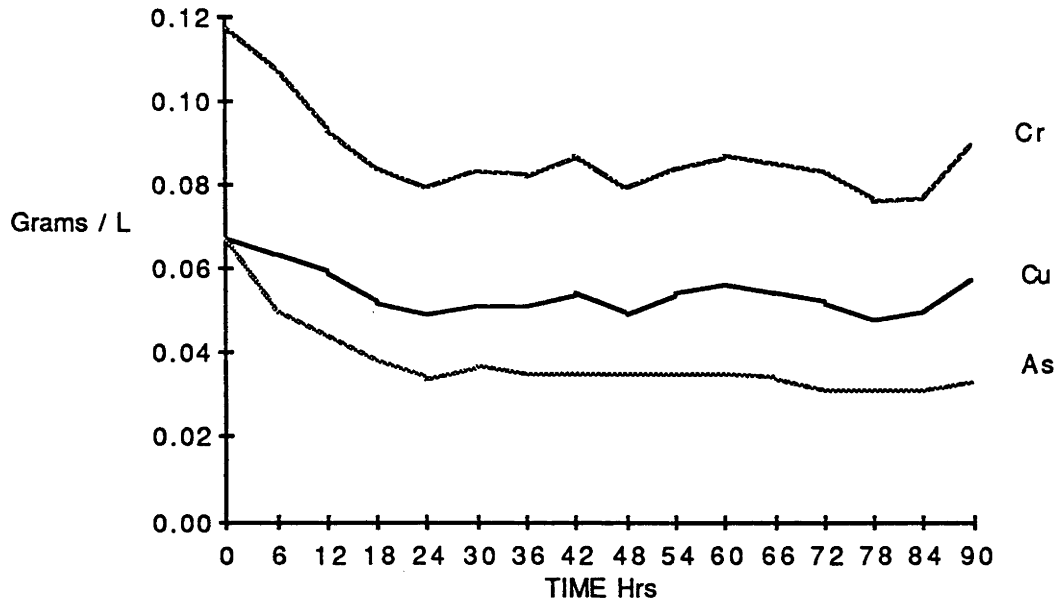


**Fig. 3-6: Movement of Cu, Cr, and As from solution during sludging**

## 3.3 General discussion:

### 3.3.1 Factors leading to sludging in treatment plants:

The results here suggest that 4 factors may be important in the formation of sludge in treatment plants; * pH of the treatment solution, the conversion of $Cr^{VI}$ to $Cr^{III}$, the complexing of $Cr^{III}$ and arsenic and chemical imbalances occurring in the treatment solution.

#### 3.3.1.1 pH:

The substantial rise in the pH of the reacted CCA solution from 2.08 to 3.26 when sludge starts to form (Fig. 3-3), is similar to that observed during the fixation of CCA to sawdust (Pizzi 1981). The latter was attributed to the removal of protons ($H^+$) from solution as a result of adsorption of chromic acid on cellulose binding sites during the initial momentary reactions (Dahlgren 1972). McNamara (1989) found that the early stages of fixation of CCA to wood involved a relatively higher loss of chromium and copper from the treatment solution due to their preferential adsorption. In contrast, the pH rise during sludging is probably due to the initial removal of relatively large quantities of chromium and arsenic from the reacted CCA solution (Fig. 3-6).

pH oscillations were also observed during conversion reactions in the fixation of CCA to wood (Dahlgren and Hartford 1972; Pizzi 1981) due to the liberation and consumption of protons as the fixation compounds become thermodynamically stable. Accordingly during sludging, the pH of the treatment solution continued to rise, although at a low rate, until sludging was essentially complete after two weeks. This suggests that as more arsenic

* In treatment plants other factors such as timber moisture content and the temperature of the CCA solution may also be important in the formation of sludge.

and chromium are removed and converted into thermodynamically stable insoluble Cr / As complexes, solution acidity decreases.

### 3.3.1.2 Conversion of $Cr^{VI}$ to $Cr^{III}$:

The study has also shown that sludging may not proceed unless some $Cr^{VI}$ has been converted to $Cr^{III}$ in the reacted treatment solution. As the concentration of $Cr^{III}$ approaches 1.5 grams $l^{-1}$ precipitation intensifies and sludge starts to form. Results here support the view that the conversion of hexavalent chrome to trivalent chrome (on the cellulose binding sites Dahlgren 1972; Dahlgren and Hartford 1972) is a major reaction leading to the primary fixation of CCA to wood.

### 3.3.1.3 Complexing of arsenic and chromium:

The importance of arsenic in sludging is indicated by its relatively higher proportion (20 %) in the sludge as compared to chromium (10 %) and copper (3 %), (table 3.3). These results support the view of Rak and Clarke (1975) that a chromium arsenic complex is likely to be the major component of sludge and that the inclusion of copper into sludge may increase (McMahon, Hill and Koch 1942) as pH of the treatment solution rises further during the sludging process (Schmalzl 1989 pers. comm.). In accord with these finding, Hager (1969) reported a better fixation of copper at high pH than at lower pH in treatment solutions. The low levels of copper in sludge suggest that copper reacts mainly with the insoluble wood components, for example, ion exchange fixation with cellulose (Dahlgren 1972; Pizzi 1981).

The concentration of arsenic in solution appears to drop more rapidly than copper or chromium during the initial stages of sludging (Table 3-3).

Sonti *et al.* (1987) also observed a drop in arsenic pentoxide in a recycled CCA treatment solution

due to preferential absorption of arsenic and also due to its precipitation. Mason and Sheard (1982) also suggested that arsenic containing CCA treatment solutions are more prone to sludging than non- arsenical formulations.

## Chapter 4

## A comparative study of the susceptibility to sludging of sulphate and oxide CCA's

### 4.0. Introduction:

Since both operational and environmental problems arise from the generation of sludge, the long term profitability of CCA wood preservatives may depend, in part, on adopting different formulations that produce less sludge. In view of the propensity of "Tanalith" CP sulphate CCA (Chapter 3) to sludge the industry in N.S.W. Queensland and the A.C.T. may have to phase out this formulation and select one that can resist sludge formation.

It has been suggested (Rak and Clarke 1975) that the chemical composition of CCA formulations may play an important role in determining its stability with respect to the formation of sludge. Hartford (1986) suggested that salt-free CCA formulations based on copper oxide may be more chemically stable and hence less susceptible to sludging than salt-type or sulphate CCA's.

In this study, the susceptibility to sludging of two of the most commonly used CCA preservatives in Australia is compared, with the primary aim of determining which is most resistant to sludge formation.

A "Tanalith" CP sulphate CCA preservative with a composition of 30% copper sulphate ($CuSO_4.5H_2O$), 38% sodium dichromate ($Na_2Cr_2O_7.2H_2O$), 17% arsenic pentoxide ($As_2O_5.2H_2O$) and 15% water ($H_2O$) and a "Tanalith" "O" Type-C oxide CCA formulation with a composition of 24% copper oxide (CuO), 40% chromium trioxide ($CrO_3$) and 36% arsenic acid ($H_4As_2O_7$) were used in the study. Sapwood and heartwood from five radiata pine trees were treated separately using a full cell treatment in a pilot

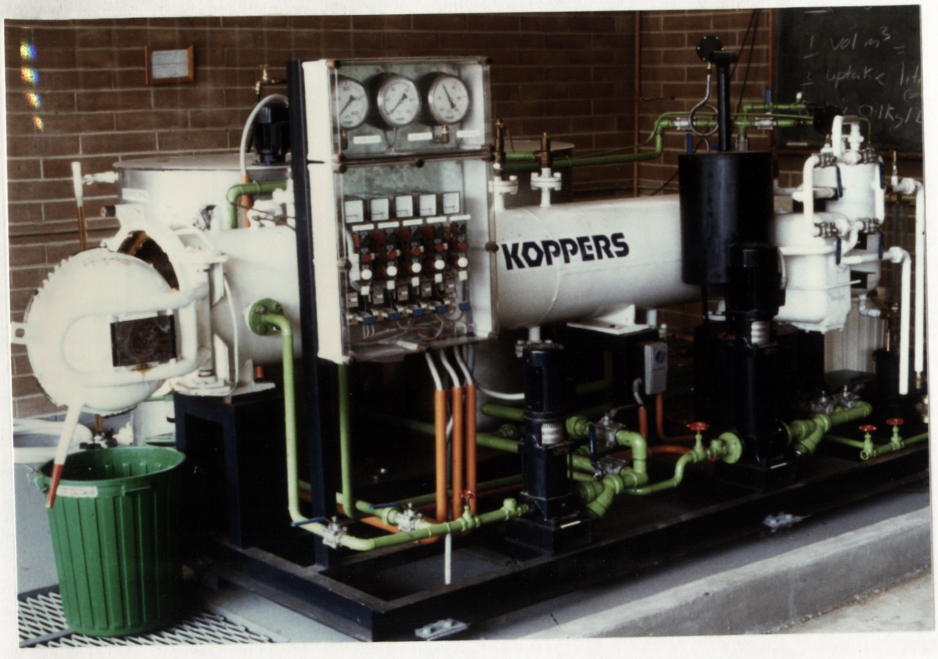


Fig. 4-1: The pilot scale treatment plant used in the treatment of timber

scale pressure plant. At the end of treatment the two formulations were compared with respect to their;

. susceptibility to sludging

. gross absorption and time to reach refusal

. surface appearance of the treated timber immediately after treatment and after 6 weeks air drying

Treatment solutions recovered after the final vacuum were collected and their susceptibility to sludging was determined by examining the following;

. changes in the pH of the recovered solution

. sludging of this solution during storage

. time required for formation of sludge

. quantity of sludge formed and

. elemental composition of the sludge

A secondary aim of the work reported here is to determine if treatment of thin (20mm) radiata pine heartwood pallings with CCA causes greater sludging in recovered solutions than treatment of sapwood pailings.

## 4.1. Materials and methods:

### 4.1.1. The pilot scale pressure plant:

The plant used for the experiments was a full cell pilot scale treatment plant (Fig. 4-1) located in the Forestry Department of the Australian National University (A.N.U.). It has a pressure cylinder 3.05 metres long and 0.46 metre in diameter with a void volume, calculated by liquid displacement, of 612 litres. The cylinder is rated for


Fig. 4-2: The differentiation of heartwood and sapwood in one of the logs from which heartwood and sapwood pallings were cut

Fig. 4-3: Boards produced from the logs by sawing around

pressures of up to 1380 kPa and vacuums of -90 kPa. Attachments to the cylinder include a pressure relief valve, a hydraulic door seal pump, a Siemens Elmo-F vacuum pump, a 2.2 kW pressure pump, a recirculation pump and two work tanks that can hold 800 litres of preservative each. The plant is manually operated by opening and shutting a series of ball valves during each phase of treatment. Preservative is mixed directly in the work tanks using an agitator. Treating liquor collecting in the sump can be pumped into a 200 litre drum for recycling.

### 4.1.2. Preparation of the timber for treatment:

Logs 3.8 metres in length and ranging in diameter from 75 cm to 86 centimetres big end diameter (B.E.D.) were cut from five 62 year old radiata pine trees growing on a recreation site at Pierce's Creek Forest, A.C.T. A series of trial runs of the pressure cylinder had indicated that a charge of 0.05 cubic metres of sawn radiata pine sapwood was the minimum required to cause substantial pH changes to CCA solutions recovered from the cylinder after treatment. Therefore, large logs were more desirable for the investigation as they ensured that there was sufficient sapwood and heartwood to ensure sludging after treatment. Five trees also ensured that any variability within trees with respect to the CCA treatment and sludging could, if necessary, be statistically examined.

After felling and four weeks air drying the extent of heartwood in the logs (Fig. 4-2) was determined by spraying freshly prepared O-anisidine solution on to the end grain of the logs. The O-anisidine solution was prepared in the laboratory by mixing a 10% (w/vol) solution of sodium nitrite ($NaNO_3$) with a solution of O-anisidine (0.5 grams of O-anisidine dissolved in 100 ml of a 1.75% (vol/vol) hydrochloric acid) (Stalker 1971). After seasoning, the logs were manually debarked before being converted to 25 mm boards by sawing around (Fig. 4-3).

Heartwood was isolated by "boxing out" the heart using a hardwood milling

Fig. 4-4: Final dressed size of pallings

Fig. 4-4
pattern. Thus sapwood and heartwood boards from each tree were clearly identified before being air dried for four weeks to below 20 % M.C. Boards were then resawn into pallings and finally dressed to a final size of 20 mm x 75 mm x 2.5 metres. Due to the relatively large sapwood band in the logs, sapwood charges averaged 0.15 cubic metres, compared to 0.08 cubic metres for heartwood (Table 4-3). Before treatment, the average moisture content of each charge was measured using a Deltron sliding hammer electrode moisture meter.

### 4.1.3. Preparation of the CCA treating solutions:

The "Tanalith" CP and "Tanalith" "O" Type-C oxide CCA solutions were prepared to achieve a minimum retention of 8.0 kg/$m^3$ and 7.0 kg/$m^3$ respectively, in accord with commercial (H4) specifications for treated radiata pine (Riley 1989)

Expected net absorption of radiata pine dried to below 25 % M.C. is 550 litres per cubic metre (Koppers - Hicksons plant operator's manual 1986) and to achieve the required retentions, the CCA solutions were prepared to the following strengths;

'Tanalith' CP sulphate CCA 8.0 kg $m^{-3}$ / 550 l $m^{-3}$ = 0.0145 kg $l^{-1}$ = 1.45 %
'Tanalith' "O" type-C oxide CCA 7.0 kg $m^{-3}$ / 550 l $m^{-3}$ = 0.013 kg $l^{-1}$ = 1.3 %

by accurately weighing 13.6 kg of the sulphate paste (80% w/w) and 9.75 kg of the oxide salts on an electronic balance (Mettler MP 15), mixing with tap water in the work tanks, and diluting to the 750 litre mark. Solution strength was measured before and after each charge using a 1.000 / 1.020 range specific

gravity hydrometer and solution temperature was determined using a thermometer. Using solution temperature and hydrometer readings, solution concentration was then obtained using a standard hydrometer chart. Solution strength was then confirmed by chemical analysis.

### 4.1.4. Treatment procedure:

The treatment used was a modified* full cell cycle with the following phases;

* (a normal Bethel treatment cycle would include a final blowback of the treatment solution after the final vacuum).

- initial vacuum of -90 kPa for 30 minutes
- flooding the cylinder while maintaining the vacuum
- applying a pressure of 1380 kPa until refusal
- blow back of the treating solution using a recirculation pump
- final vacuum of -90 kPa for 30 minutes.

Information relevant to the treatment including charge volume, moisture content and gross absorption, was recorded in charge reports (Table 4-3). After treatment the timber was placed on a drip pad for 24 hours before being air dried for six weeks. 19 charges were run; five charges of each of sapwo and heartwood using sulphate CCA and five charges of sapwood and four of heartwood using oxide CCA. There was insufficient heartwood to run five charges using the oxide CCA.

### 4.1.4. Laboratory investigations of sludging in treatment solutions:

Trial treatment runs had shown that charges of sawn radiata pine up to 0.05 cubic metres did not give sufficient volumes of post treatment drips for analysis of sludging in solutions. Therefore examination of sludging was based on treatment solutions that had been extracted by the final vacuum. This solution was drained from the pressure cylinder, transferred to 50 ml

graduated plastic sample tubes (Opticul 2070 polypropylene tubes) and then examined in the laboratory. The method used is similar to that described in Section 3.1.

## 4.2. Results:

### 4.2.1. Sludging of CCA solutions after treatment of sapwood:

Sludge formed between six and eight weeks in all the sapwood charges treated with the sulphate CCA wood preservative. All charges (Tree 1 - Tree 5) produced on average, 0.30 grams of sludge per litre of treating solution (Table 4-1). Sludging was preceded by a turbidity of the solution in the tubes. This increased before deposition of sludge occurred at the base of the tubes. In contrast, charges of sapwood (Tree 1 - Tree 5) that were treated with the oxide CCA treatment solution remained free of sedimentation and sludge.

#### 4.2.1.1. pH changes:

Average pH at the sludging point was 2.34, a pH rise of some 0.33 above the initial solution pH (Table 4-1). In contrast, with the oxide CCA there was an average pH increase of only 0.22 after treatment.

The rise in pH may be related to the quantity of sludge formed (Table 4-1). Sapwood of Trees 2 and 3 which caused more extensive pH rises in the sulphate CCA solutions also generated more sludge than the other trees. Similarly, tree 5 which caused the least effect on solution pH produced smaller amounts of sludge.

#### 4.2.1.2. Conversion of $Cr^{VI}$ to $Cr^{III}$:

Initial determinations of $Cr^{III}$ gave very low readings perhaps due to the relatively slow conversion of $Cr^{VI}$ to $Cr^{III}$. Hence this analysis was not undertaken on recovered solutions.

**Table 4-1: Effects of sapwood on the sludging of sulphate and oxide CCA**

| Tree No | Sulphate CCA | | | Oxide CCA | | |
|---|---|---|---|---|---|---|
| | pH before treatment | pH at sludging | Wt of sludge (Grams/ l ) | pH before treatment | pH at sludging | Max pH |
| 1 | 2.04 | 2.37 | 0.27 | 1.73 | DNS | 2.01 |
| 2 | 1.98 | 2.34 | 0.40 | 1.76 | DNS | 2.03 |
| 3 | 2.02 | 2.38 | 0.39 | 1.74 | DNS | 1.97 |
| 4 | 2.00 | 2.33 | 0.23 | 1.76 | DNS | 1.91 |
| 5 | 2.02 | 2.29 | 0.20 | 1.76 | DNS | 1.94 |
| Mean | 2.01 | 2.34 | 0.30 | 1.75 | DNS | 1.97 |
| SDev | 0.02 | 0.04 | 0.09 | 0.01 | * | 0.05 |

DNS = did not sludge

### 4.2.2. Chemical composition of the sludge from sapwood:

Sludge formed after treatment of sapwood had an elemental composition of 41.4% As, 19.7% Cr, 3.2% Cu (Figure 4-1) and 35.7 % possibly of sulphate and oxalates salts. However, there was variation among the five trees in the relative levels of arsenic in the sludge, i.e., Tree3 > Tree2 > Tree4 > Tree5 > Tree1. This is similar to the variation in the maximum pH and the quantity

of sludge formed (Table 4-1). With the exception of Tree 1 the chromium content of the sludge is the same for all trees. The level of copper is low and does not vary greatly between trees. In accord with the findings in Chapter 3 and also those of Cokley and Smith (1965) sludge appears to be largely composed of arsenic and chromium with little copper present.

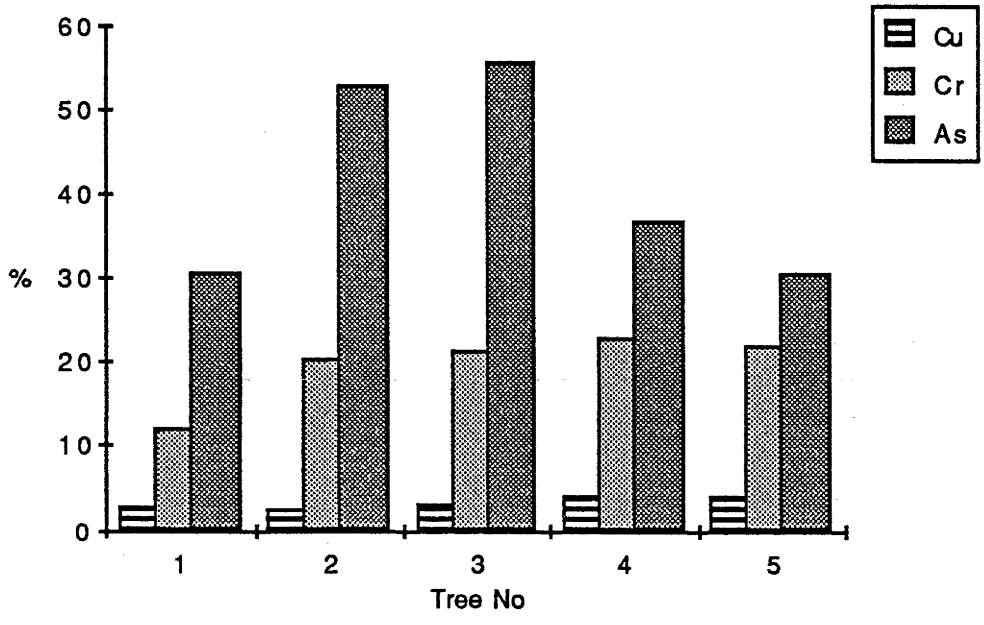


**Fig. 4-5: Variation in the composition of sludge from sapwood**

### 4.2.3. Sludging of CCA solutions after treatment of heartwood:

For tree 4 the treatment of heartwood with the sulphate CCA solutions caused sludge formation in recovered CCA solutions after four weeks of storage (Table 4-2). pH at sludging was the same as for the sulphate CCA treatment of sapwood from Tree 3 (2.38) (Table 4-1). However, no sludging occurred in recovered solutions from the other sulphate or oxide CCA

treatments of heartwood despite a significant change in pH of both CCA solutions (Table 4-2). This could be due to the following;

(a) Heartwood of Tree 4 had been treated in the autumn immediately after the sapwood charges when the treating temperature averaged 16.4 °C. All other heartwood charges were treated in the winter when the treating temperatures were 11.2 °C. Possibly the lower treating temperature may have reduced the initial rate of reaction of heartwood extractives with the sulphate CCA solution.

(b) The laboratory temperature had also dropped from 19 °C to 17 °C when the heartwood charges were treated. Again these relatively lower temperatures may also have caused the reaction between heartwood extractives and CCA to proceed at a lower rate than sapwood.

(c) Alternatively, heartwood charges averaged 0.08 $m^3$ approximately half those used for the treatment of sapwood where average charge volume was 0.15 $m^3$ (Table 4-3). It is possible that lower wood volumes and presumably lower soluble extractives entering the treatment solutions could have reduced the tendency of CCA solution to form sludge.

**Table 4-2: Effects of heartwood on pH and sludging of recovered CCA solutions**

| Tree No | Sulphate CCA | | | Oxide CCA | | |
|---|---|---|---|---|---|---|
| | Nominal pH | pH at sludging | Max pH | Nominal pH | pH at sludging | Max pH |
| 1 | 2.02 | DNS | 2.22 | 1.75 | DNS | 1.92 |
| 2 | 2.02 | DNS | 2.11 | 1.76 | DNS | 1.86 |
| 3 | 2.02 | DNS | 2.10 | 1.78 | DNS | 2.00 |
| 4 | 2.02 | 2.38 | 2.43 | * | * | * |
| 5 | 2.02 | DNS | 2.14 | 1.81 | DNS | 1.93 |
| Mean | 2.02 | * | 2.14 | 1.78 | * | 1.93 |
| SDev | 0.00 | * | 0.05 | 0.03 | * | 0.06 |

DNS = Did not sludge

### 4.2.4. Gross absorption of CCA by sapwood and heartwood:

Gross absorption is an indicator of the extent of penetration and distribution of CCA at the end of the pressure phase of the treatment cycle (Wilkinson 1979; Kumar and Morrel 1989). It includes both the CCA absorbed during

flooding of the cylinder and that injected as a direct result of applied pressure. Maximum possible absorption for any given timber species is governed by wood void volume and hence density which can be determined from the following expression;

**Void volume ($m^3$) = 1000 - BD/1.5**

(where BD = basic density) Koppers-Hickson (1986)

For example, radiata pine from the ACT region has an average basic density of 404 kg $m^{-3}$.

Void volume is also dependent on moisture content (MC), maximum possible absorption being expressed as;

$$\textbf{Absorption (l)} = 1\,000 \left[ \frac{\textbf{BD}}{\textbf{100}} \times ( 66.7 + \textbf{MC} ) \right]$$

Koppers-Hickson (1986)

Below fibre saturation point (about 30% MC), gross absorption for radiata pine can in theory exceed 610 litres $m^{-3}$. In practice, however, gross absorption of CCA preservative is much lower due, in part, to anomalies in the microscopic structure of the wood, the presence of untreatable knots, and heartwood, and finally air and resins that can prevent the uptake of solution.

Net dry salt retention (NDSR) is a measure of the weight of salts remaining in the wood after treatment. It is dependant on net absorption or the quantity of preservative left in the timber at the end of the cycle and also on

the strength of the treating solution. In practice net absorption for radiata pine in the A.C.T. averages 550 litres $m^{-3}$.

NDSR can be expressed as;

**NDSR (kg $m^{-3}$) = net absorption (l $m^{-3}$) x solution strength (kg $l^{-1}$)**

Table 4-3 shows that higher average gross absorptions in sapwood were achieved with the oxide CCA treatments than the sulphate CCA. In this experiment sawn heartwood was as readily treated as sapwood. This is unusual, (normally radiata pine heartwood is difficult to treat with CCA by norm pressure treatment methods), and may be related to the thin size of sections treat With the oxide CCA treatment, heartwood absorbed more treatment solution (751 l $m^{-3}$) than sapwood (708 l $m^{-3}$).

Following treatment wood was air dried for six weeks. Timber treated with sulphate CCA solution turned a light green colour and also showed surface deposits of a white salt that could be easily washed off. These deposits may have been sodium sulphate ($Na_2SO_4$) which is reported to occur on wood surfaces after treatment with sulphate CCA (Hartford 1986). The oxide CCA treated timber was initially a distinct and aesthetically appealing light brown colour with no surface deposits, however after 10 weeks the oxide treated wood also acquired a green coloration similar to that of CCA sulphate treated wood.

**Table 4-3: Summary of charge reports**

| | Sapwood | | | | | | Heartwood | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tree No | Sulphate CCA | | | Oxide CCA | | | Sulphate CCA | | | Oxide CCA | | |
| | Vol. (m3 ) | M.C. (%) | ABS. (l m-3) | Vol. (m3) | M.C. (%) | ABS. (l m-3) | Vol. (m3) | M.C. (%) | ABS. (l m-3) | Vol. (m3) | M.C. (%) | ABS. (l m-3) |
| 1 | 0.13 | 14.0 | 716 | 0.13 | 15.0 | 793 | 0.08 | 16.7 | 590 | 0.08 | 16.0 | 629 |
| 2 | 0.16 | 14.0 | 679 | 0.12 | 15.0 | 723 | 0.08 | 17.6 | 613 | 0.08 | 16.1 | 670 |
| 3 | 0.14 | 15.0 | 713 | 0.13 | 15.9 | 677 | 0.08 | 17.2 | 667 | 0.07 | 16.4 | 853 |
| 4 | 0.14 | 14.3 | 610 | 0.11 | 15.4 | 670 | 0.08 | 19.0 | 658 | * | * | * |
| 5 | 0.18 | 15.0 | 632 | 0.12 | 16.1 | 678 | 0.06 | 17.6 | 694 | 0.08 | 16.3 | 853 |
| mean | 0.15 | 14.5 | 670 | 0.12 | 15.5 | 708 | 0.08 | 17.6 | 644 | 0.08 | 16.2 | 751 |
| sdev | 0.02 | 0.51 | 47.7 | 0.01 | 0.51 | 51.9 | 0.01 | 0.86 | 42.1 | 0.01 | 0.18 | 118.7 |

## 4.3. General discussion:

Four findings are apparent from this study. These are;

(a) The oxide CCA was more resistant to sludging than the sulphate CCA when used to treat radiata pine sapwood in a pilot scale full cell treatment plant (Table 4-1).

(b) The quantity of sludge formed in the recovered CCA treatment solution appears to bear some relationship to the pH of the solution.

(c) The sludge formed is composed of 41 % arsenic, 20 % chromium, 3 % copper and 36 % salts, possibly sulphate and oxalates. This sludge is similar to that produced in commercial treatment plants (Section 3.2.3) except that the arsenic and chromium levels are relatively higher. However, the level of arsenic in the sludge varied between trees (Fig. 4-1), in accord with the findings of McCarthy and Wilson (1957) that fixation of arsenic varied considerably in radiata pine.

(d) Heartwood of radiata pine with the exception of tree 4 appears to be more resistant to sludging than sapwood. This result may be due to a greater concentration of CCA soluble extractives in the sapwood than in the heartwood. Alternatively sapwood extractives may be more reactive than those found in heartwood.

### 4.3.1. Factors that may cause CCA's to resist sludging:

From the results here it is apparent that the oxide CCA is more resistant to sludging than the sulphate CCA when used to treat radiata pine sapwood in a pilot scale treatment plant (Table 4-1). This may be due to the following factors;

#### 4.3.1.1. pH:

The relatively lower initial pH of the oxide CCA treatment solution (1.75) may be responsible for its relatively greater resistance to sludging since the increase in pH of recovered CCA solutions appears to be related to the extent of sludging (Table 4-1). This finding is in accord with the conclusions of the 'Special Task Force On Sludging' (Hartford 1986) that the more acidic CCA's tend to resist sludging.

#### 4.3.1.3 Duration of treatment:

Timber treated with the oxide CCA took less time to reach refusal than timber treated with the sulphate CCA. Sludging is thought to be proportional to duration of treatment (Pizzi *et al.* 1984; Hartford 1986). Hence less sludging with oxide CCA may be related to the shorter treatment times.

### 4.3.2. Other differences:

#### 4.3.2.1. Gross absorption:

Both radiata pine sapwood and heartwood absorbed more oxide CCA than sulphate CCA solution (Table 4-3).

This result suggests that the greater acidity of the oxide CCA may cause increased dissolution of extractives blocking flow paths within the wood. In

contrast the relatively lower gross absorption of sulphate CCA may be due to sedimentation and/or suspension of the CCA which could block wood flow paths.

Oxide CCA formulations are generally associated with deeper penetration in comparison to sulphate CCA (Watson 1966; Kumar and Morrel 1989) so that oxide CCA probably provides better protection of radiata pine than sulphate CCA. In commercial practice, lower retentions are required for oxide CCA treatments (7 kg $m^{-3}$) than sulphate CCA (10 kg $m^{-3}$) for H4 ground contact treatment of radiata pine. Thus weaker solutions of oxide CCA are used (1.3%) than sulphate CCA (1.8 %), for treatment of radiata pine to H4 hazard level but this is not reflected by cost savings since it is more costly to treat with an oxide CCA (about \$32.00 $m^{-3}$) than a sulphate CCA (about \$25.00 $m^{-3}$) (Riley 1989 pers. comm.).

Oxide CCA is also thought to fix more readily to timber than sulphate CCA (Eadie and Wallace 1962; Pizzi 1983) due to lower pH and has a relatively higher performance index (0.2876) against wood decay fungi, especially at a composition of 24 % $As_2O_5$, 34 % $CrO_3$ and 42 % CuO (Hartford *et al.* 1982).

# CHAPTER 5

## A laboratory study of susceptibility to sludging of sulphate and oxide CCA's

### 5.0. Introduction:

Treating temperature and storage temperature are thought to be important factors determining the susceptibility to sludging of a recycled CCA treatment solution such that seasonal variation in the extent of sludging can be expected from a treatment plant (Cokley and Smith 1965; Wilkinson 1979; Hartford 1986). In the comparative study (Chapter 4) the treating temperature fell from an average of 16.4 °C during the sulphate CCA treatment to an average of 11.2 °C during the oxide CCA treatment (Section 4.2.3 (a)) and the laboratory temperature also fell from 19 °C to 17 °C during storage of the reacted CCA's (Section 4.2.3 (b)). To eliminate the possibility that treating and storage temperature greatly affected the finding (Chapter 4) that the oxide CCA was less susceptible to sludging than the sulphate CCA an experiment was undertaken to compare their susceptibility to sludging under controlled laboratory conditions.

The aim of this chapter is therefore to consolidate the findings reported in Chapter 4 that oxide CCA appears to be less susceptible to sludging than sulphate CCA. The choice of materials is in accord with the model experiments carried out to investigate the precipitation of CCA using AnalaR grade D(+) glucose (Rak and Clarke 1975), and ethanol (Schmalzl 1989 pers. comm.).

## 5.1. Materials and methods:

A 1.45% CCA solution was prepared and transferred to two separate 1 litre volumetric flasks. 20 grams of AR D(+)-glucose was then added to one flask and 5 mLs of ethanol (100% v/v) was added to the other flask. These solutions were diluted to the mark with tap water and then mixed well by shaking the flasks. Two 1.3% oxide CCA solutions were also prepared in a similar way using glucose or ethanol.*

1000 mls of each solution was then transferred separately to two 1000 ml graduated beakers, 2 x 1000 mls of sulphate CCA solution and 2 x 1000 mls of oxide CCA solution in four 1000 ml beakers. The beakers were then placed in a water bath at a constant temperature of 25 °C in a fume cupboard. The temperature of the water bath and the CCA solutions was monitored using thermometers placed in each beaker and in the water bath. The fume cupboard was completely covered with black polythene to exclude any effects light may have on the reduction of $Cr^{VI}$ to $Cr^{III}$. A piece of polythene was also used to cover the beakers to minimize the loss of preservative solution due to evaporation.

pH measurements were taken every two days and $Cr^{III}$ strength determined every two days by U.V. spectroscopy using the method described in Section 3.1. The sludging point for the reacted CCA solutions was noted and the sludge was collected after 3 weeks by decanting the top solution then washing the sludge with distiled water. The wet sludge was then placed in a petri dish and allowed to evaporate at room temperature. The dry sludge was placed in a desiccator over anhydrous sodium chlorite crystals and kept under vacuum for twenty four hours for dry weight determinations.

*CCA controls containing no glucose or ethanol were not included in the experiment since it is well established that uncontaminated CCA solutions are stable and will not form sludge unless organic compounds (reducing agents) are added.

## 5.2. Results:

Sludge formed when both the sulphate CCA and oxide CCA were reacted with D(+)-glucose and ethanol but less sludge was formed in the oxide CCA than sulphate CCA (Table 5-1). After addition of D(+)-glucose the sulphate CCA took 10 days to sludge whereas sludging occurred in the oxide CCA after 12 days. Similarly after addition of ethanol the sulphate CCA formed sludge after 14 days whereas sludging occurred in the oxide CCA after 16 days (Table 5-2). After three days of reaction a heavy turbidity occurred in the sulphate CCA which intensified towards the precipitation point. In contrast, the oxide CCA remained clear and the production of sludge only occurred after 9 days of reaction.

In both glucose treatments the dry sludge consisted of green flakes but those from the oxide CCA were much bigger than from the sulphate CCA. In contrast the sludge formed from ethanol treatments was a brown colour. Sludge obtained from hot water extraction of spotted gum (Cokley and Smith 1965) was also reported to have a brown coloration.

### 5.2.1. Effect of D(+) glucose and ethanol on CCA's:

#### 5.2.1.1. pH:

Addition of D(+)-glucose to the sulphate CCA and oxide CCA solutions caused a rise in pH of 0.39 and 0.50 respectively (Table 5-1). This result suggests that D(+)-glucose was more effective in raising the pH of the oxide CCA than the sulphate CCA. Despite this effect, the pH at which sludge formed was higher for the sulphate CCA (2.25) than the oxide CCA (2.19). In addition, pH continued to rise steadily in the sulphate CCA during sludging while pH for the oxide CCA appeared to have stabilized after 18 days of reaction (Fig. 5-1).

The effects of ethanol on pH were similar for both sulphate CCA (0.30) and oxide CCA (0.31) but pH at sludging was also higher in the former (2.16) than the latter (2.00). These results may be related to the findings reported in Section 4.2.1.1 that pH appears to be correlated with the quantity of sludge generated.

### 5.2.1.2. Conversion of $Cr^{VI}$ to $Cr^{III}$ in the treatment solutions:

D(+)-glucose produced more $Cr^{III}$ in the sulphate CCA (1.15 grams $l^{-1}$) than oxide CCA (0.62 grams $l^{-1}$) (Table 5-2). Similarly ethanol also produced more $Cr^{III}$ in the sulphate CCA (0.58 grams $l^{-1}$) than the oxide CCA (0.43 grams $l^{-1}$).

### 5.2.1.3. Quantity of sludge formed:

The D(+)-glucose / sulphate CCA mixture generated more sludge (3.17 grams) than the D-glucose / oxide CCA mixture (2.93 grams) (Table 5-1). Similarly the ethanol / sulphate CCA reaction also generated more sludge (1.74 grams) than the ethanol / oxide CCA reaction (0.74 grams).

**Table 5-1: Effect of D(+)-glucose and ethanol on the pH of sulphate and oxide CCA's:**

| Reducing agent | Sulphate CCA* | | | Oxide CCA* | | |
|---|---|---|---|---|---|---|
| | Initial pH | pH at Sludging | Wt. of sludge (g) | Initial pH | pH at sludging | Wt. of sludge (g) |
| 2% D-glucose | 1.86 | 2.25 | 3.17 | 1.69 | 2.19 | 2.93 |
| 0.5% Ethanol | 1.86 | 2.16 | 1.74 | 1.69 | 2.00 | 0.74 |

*Results are the average for the two replicates

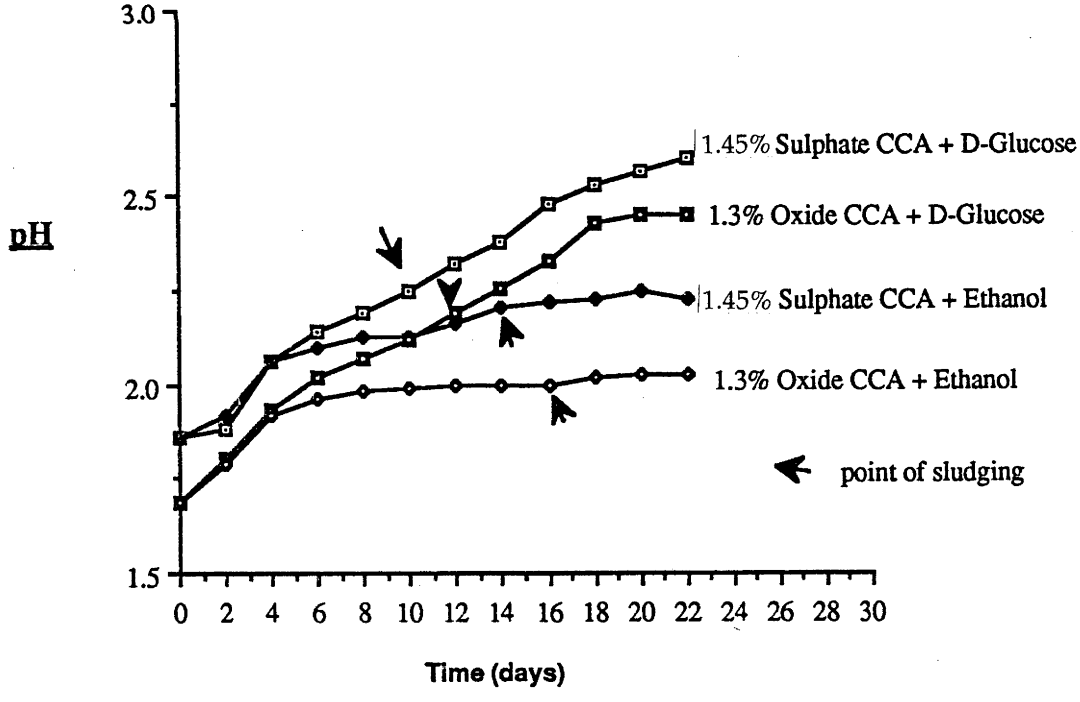


**Fig. 5-1: pH changes and point of sludging in the sulphate and oxide CCA solutions after addition of glucose and ethanol.**

**Table 5-2 : Yield of $Cr^{III}$ with D(+)-glucose and ethanol**

| Reducing agent | Sulphate CCA * | | | Oxide CCA * | | |
|---|---|---|---|---|---|---|
| | Cr III @ 1 week (grams/l) | Cr III @ sludging (grams/l) | Time to sludge (days) | Cr III @ 1 week (grams/l) | Cr III @ sludging (grams/l) | Time to sludge (days) |
| 2% D-glucose | 0.50 | 1.15 | 10 | 0.33 | 0.62 | 12 |
| 0.5% Ethanol | 0.38 | 0.58 | 14 | 0.13 | 0.43 | 16 |

*Results are the average for the two replicates

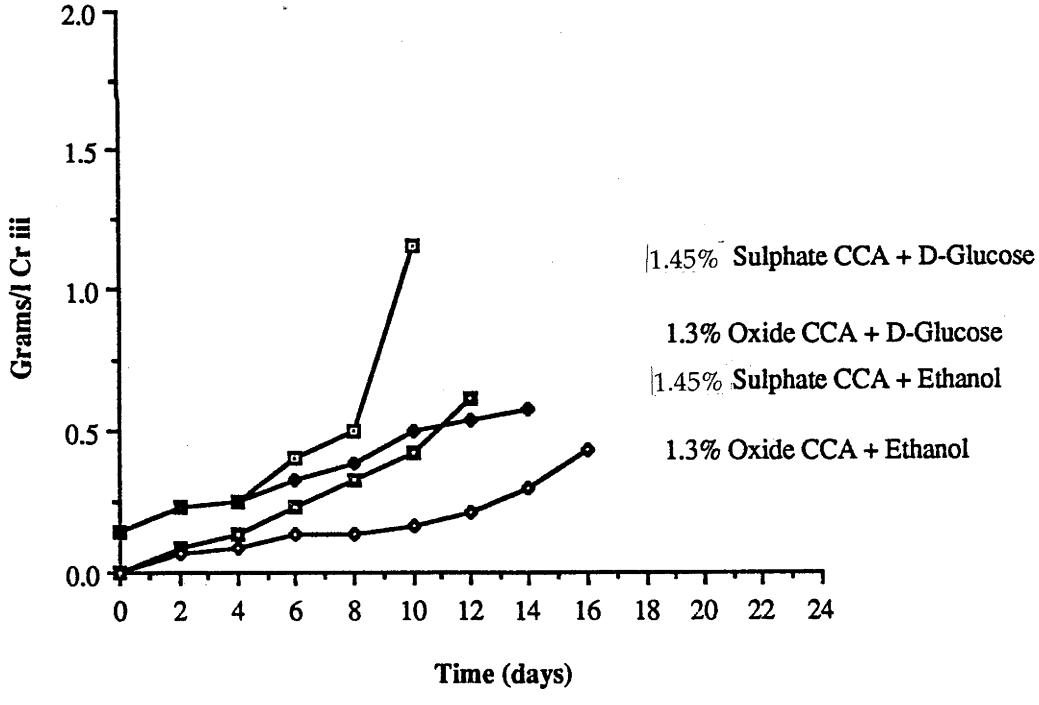


**Fig. 5-2: Conversion of $Cr^{VI}$ to $Cr^{III}$:**

## 5.3. Discussion:

### 5.3.1. Susceptibility to sludging of oxide and sulphate CCA:

Under controlled laboratory conditions the sulphate CCA sludged more rapidly and generated more sludge than the oxide CCA confirming that the oxide CCA is less susceptible to sludging. This study also showed that given sufficient reducing material in solution, the oxide CCA will also sludge and that sludging of the oxide CCA may commence at a pH as low as 2.00 (Table 5-1). The rate at which sludge formed was similar for each treatment solution (Fig. 5-1) suggesting that a difference in pH may explain the major difference in susceptibility to sludging between the sulphate CCA and the oxide CCA in accord with the finding of Hartford (1986). The greater resistance to sludging of the oxide CCA is also demonstrated by the cessation of sludging as indicated by a constant pH after 18 days of reaction with D(+)-glucose. In contrast sludging continued to progress normally in the sulphate CCA / D(+)-glucose reaction beyond 18 days. If reactions were allowed to continue for longer than 3 weeks it appears that the quantity of sludge formed from the reaction of D(+)-glucose and sulphate CCA could have been even greater. In addition sulphate CCA tends to form sediment more easily than oxide CCA. Sedimentation of a CCA preservative during storage is not desirable and can lead to the formation of sludge (Schmalzl 1989 unpublished report)

The concentration of $Cr^{III}$ in the D(+)-glucose / sulphate CCA reaction (1.15 grams $l^{-1}$) is close to that observed in commercial treatment (1.5 grams $l^{-1}$) and the green sludge obtained also resembled that generated in commercial treatment of radiata pine (Section 3.2.1). These findings also suggest that simple sugars such as glucose may play a major role in the reactions leading to sludging in the treatment of radiata pine.

# CHAPTER 6

## Conclusions, general discussion and suggestions for further research

### 6.1. Quantitative analysis of sludging in a commercial treatment plant:

An important finding of this study is that the collection and analysis of drips from radiata pine treated with a CCA wood preservative is a suitable method for the examination of sludge formation in treatment plants. Sludge formation appears to be preceded by extensive chemical reactions between the CCA solution and the acid soluble wood components which raise the pH of the treating solution in a similar manner to that described by Dahlgren (1972) and Pizzi (1981) in their work on fixation. The soluble wood components probably reduce $Cr^{VI}$ to $Cr^{III}$. The $Cr^{III}$ ions in solution then react with arsenic to form an insoluble chromium arsenate complex which precipitates as sludge.

It appears therefore, that the chemical reactions leading to sludge formation are similar to fixation so that the description (Hartford 1986) that "sludge formation is a fixation of CCA outside wood" is perhaps fitting. However, there are two exceptions; firstly, copper is not fixed in sludge whereas in wood it is thought to be bonded to the cellulosic components of wood by ion exchange fixation (Dahlgren 1972; Dahlgren and Hartford 1972; Pizzi 1981) and secondly, conversion reactions in the sludge have not been identified.

In this study, under commercial treatment of radiata pine, sludging occurs when pH and $Cr^{III}$ ions reach a threshold level of 3.26 and 1.5 grams $l^{-1}$

respectively, but some sludging may also occur at a pH and $Cr^{III}$ strength as low as 2.00 and 0.43 grams $l^{-1}$ respectively. pH and $Cr^{III}$ strength may thus be used as indicators of the susceptibility to sludging of a recycled CCA treating solution, but probably cannot predict precisely the point at which sludging will occur. Of the total sludge formed here, 60 % was formed within 48 hours of treatment. The sludge formed contained high levels of arsenic (20%) and chromium (10 %) and relatively low levels of copper (3 %). The remaining components of the sludge (67%) were probably salts, possibly oxalates.

## 6.2. Comparative susceptibility to sludging of oxide and sulphate CCA's

Oxide CCA appears to be more resistant to sludging than sulphate CCA after treatment of radiata pine sapwood. The oxide CCA is more stable with respect to pH changes, and extent of sludging than the sulphate CCA, but will, given sufficient reducing material present in the solution, sludge. The lower initial pH of the oxide CCA treatment solution (1.75) may be responsible for its greater resistance to sludging since pH appears to be related to the extent of sludging. Conversely the higher initial pH of the sulphate CCA treatment solution (2.02) may be responsible for its lower resistance to sludging.

The results from one charge indicated that heartwood of radiata pine may cause more sludging than sapwood when treated with sulphate CCA but further research is needed to clarify this point. Treatment of radiata pine heartwood with the oxide CCA caused a greater pH rise (0.15) than sulphate

* Lack of time prevented work being undertaken to determine whether oxide CCA causes more sludging with heartwood than sulphate CCA. This is an area worthy of further research.

CCA (0.12) suggesting that oxide CCA may cause more sludging when used to treat heartwood than sulphate CCA. This difference could be due to the greater acidity of the oxide CCA which may dissolve more of the CCA soluble components in heartwood than could be achieved by the less acidic sulphate CCA solution.*

## 6.3. General discussion:

### 6.3.1. Control of sludging:

This study suggests that the reactions leading to sludging are dependent on the conversion of $Cr^{VI}$ to $Cr^{III}$ as a result of the reaction between CCA and soluble wood components and the complexing of $Cr^{III}$ with arsenic to form insoluble chromium/arsenic complexes. The rise in pH is a reflection of the extent of the removal of $Cr^{VI}$ and arsenic from the reacted CCA solution. As arsenic is the main component of sludge, these findings also indicate that as long as the CCA solution contains $Cr^{III}$ ions, arsenic will be removed from solution and sludge will form.

It is probable that the treatment solution removed by the final vacuum is largely responsible for the problem of sludging. Results here for radiata pine, have shown that a charge of about 18 cubic metres of round timber, when treated by a sulphate CCA solution at a temperature of 20 °C will cause the solution removed by the final vacuum to sludge in 6 hours at a pH of about 3.26 and a $Cr^{III}$ strength of 1.5 grams $l^{-1}$. These threshold levels and time required to sludge may vary for different wood species, different charge sizes and different treating temperatures. For example, in the treatment of Mexican weeping pine (*Pinus patula* Schiede and Deppe), sludge was noticed after 24 hours of storage (Pizzi *et al.* 1982). Under commercial practice in the U.S.A., sludge is reported to form at a pH of approximately 2.3 (Hartford 1986).

Of the total sludge formed in eight weeks (from a commercial plant), about 60% was generated in the first 48 hours following treatment (Fig. 3-4). The process of sludge formation was complete after 2 weeks (Fig. 3-5) which is similar to the times required for complete fixation of CCA (Dahlgren 1972; McNamara 1989). This finding is important for the control of sludging. Within the normal operating procedure in a treatment plant, three options exist by which sludge may be minimized *(Other options may also exist)

(a) Modifying the treatment schedule by shortening or eliminating the final vacuum phase,

(b) isolating the treating solution removed by final vacuum after each charge so that pH and $Cr^{III}$ content and sludge formation can be monitored before recycling and

(c) using oxide CCA preservative solution in place of sulphate CCA.

The elimination of the final vacuum has been tried on a commercial basis in South Africa for the treatment of flooded gum (*Eucalyptus grandis* Hill ex Maiden) poles (Pizzi *et al.* 1984). Advantages of this technique are reported to be:

. less sludging problems

. no loss of usable preservative to sludge

. a more efficient treatment process

. a shorter treatment cycle and hence increased plant throughput

. fewer stoppages due to regular cleaning of equipment

. no capital expenditure on new equipment

However, elimination of the final vacuum may cause excessive post treatment bleeding of preservative that may affect the quality of the product by depositing salts on the surface of timber and also cause handling problems. These problems can be largely solved by kiln drying of the treated timber. Kiln drying also has the additional advantage of ensuring total fixation of the preservative in a short time to eliminate the risk of leaching of unfixed salts during wet weather. Post treatment drying of CCA treated timber to accelerate fixation is rapidly gaining acceptance in Europe.

Treatment solution removed by the final vacuum can also be pumped into temporary storage tanks where its elemental balance and initial pH can be restored by "reconditioning" with arsenic pentoxide ($As_2O_5.2H_2O$) and potassium dichromate ($K_2Cr_2O_7.2H_2O$) before recycling it back to the work tanks. In addition the treating solution can be filtered using a 25 or 50 micron filter attached to the recirculation line as this would also filter all solution returning to the work tanks including solution from the "kick back".

Perhaps the most effective way of controlling sludging of the CCA treatment solution, as shown by this study, is to use the oxide CCA formulation. Oxide CCA preservative appears to resist sludging because of its lower pH and has less tendency to separate or form sedimentation during storage. Furthermore, it was shown that the oxide CCA penetrated thin radiata pine sapwood and heartwood pallings to a greater extent than sulphate CCA which is an additional beneficial aspect of the use of oxide CCA.

Oxide CCA solutions are also known to fix readily to timber (Eadie and Wallace 1962; Pizzi 1983) and perform better against decay fungi than sulphate CCA (Hartford *et al.* 1982). They are also reported to reduce the electrical conductivity of treated poles (Clarke and Donaldson 1969) and do not corrode treatment plant equipment and galvanized hardware (Taylor 1981) unless the pH is below 1.67 (Hartford 1986). Since oxide CCA preservatives cost more to use ($32.00 per $m^{-3}$ of treated radiata pine) than sulphate CCA ($25.00 $m^{-3}$) these advantages may need to be balanced against the additional cost of using this formulation.

### 6.3.2. Environmental implications of CCA treatments:

Sludge formed during commercial treatment of radiata pine is toxic as it contains up to 30 % arsenic. If not washed thoroughly the sludge may also contain the toxic and very soluble $Cr^{VI}$. The current method of disposing of sludge by encapsulating it in concrete may require changing since concrete is porous and $Cr^{VI}$ could conceivably be leached from the concrete matrix. The use of oxide CCA may reduce the volume of sludge generated in a treatment plant but as mentioned earlier (Section 6.3.1), this preservative is more expensive to use compared to sulphate CCA. Treatment costs may, therefore, need to be compared with the costs of sludge disposal, the loss of usable preservative caused by sludge formation and also the possible social costs arising from pollution of the environment. Once these additional costs are included, the oxide CCA preservatives may be more financially attractive than their sulphate counterparts. In addition, the long term acceptance of CCA wood preservatives may depend on their environmental acceptance.

Under the US Environmental Protection Agency regulation on "effluent from wood treating plants" (Winandy 1983), sludge must contain a

maximum proportion of 4 PPM As, 4 PPM Cr and 5 PPM Cu. These figures can be put into perspective by considering that soils in the U.S.A. can contain as much as 40 PPM arsenic (Price 1978) and a therapeutic dose for an adult human is 0.5 mg of As , similar to the arsenic that may be ingested during an average dietary consumption of seafood (Johanson and Dale 1973). Although soils, particularly with a high content of iron, aluminium and exchangeable calcium have a marked absorptive capacity for arsenic compounds such as arsenates, tests involving CCA treated poles in service for 32 years showed that no arsenic had leached to the surrounding soil (Price 1978). While it may be safe to assume that the arsenic contained in sludge is fixed as an insoluble metal salt complex similar to that in wood, the fact that sludge contains 20 % of arsenic and some hexavalent chromium ($Cr^{VI}$) may require that the current concrete encapsulating disposal technique be reviewed.

### 6.4. Suggestions for further research:

Strictly speaking, this study is only pertinent to the treatment of radiata pine with CCA. Wider application of the findings may depend on further studies of other species such as spotted gum. Additional studies could include a comparison of the effect of variation in the oxide CCA formulations on sludging. A study could also be conducted to determine variation in the extent of sludging between sapwood and heartwood when treated with oxide CCA.

From an environmental view point, it may be important to study the effectiveness of current disposal methods of sludge, particularly the leachability of sludge from concrete. These studies could include leaching tests on concrete encapsulated sludge in order to select the most effective

proportion of cement, sand and sludge that would ensure that the latter is not leached from the mineral matrix into the environment.

Other studies could also continue the search for suitable methods to convert sludge to usable preservative. For example, in developing countries where environmental regulations are different to those in Australia, sludge could find use in various applications such as in the foundations of buildings to protect them against termite attack or alternatively as an insecticide. After all, sludge contains three of the most effective chemicals known to protect timber from degrading organisms.

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